

Monocyclopentadienyl complexes

5 The present invention relates to monocyclopentadienyl complexes in which the cyclopentadienyl system bears at least one unsubstituted, substituted or fused, heteroaromatic ring system bound via a specific bridge and to a catalyst system comprising at least one of these monocyclopentadienyl complexes, and also to a process for preparing them.

10 In addition, the invention relates to the use of the catalyst system for the polymerization of copolymerization of olefins and to a process for preparing polyolefins by polymerization or copolymerization of olefins in the presence of the catalyst system and to polymers obtainable therewith.

15 Many of the catalysts which are used for the polymerization of α -olefins are based on immobilized chromium oxides (cf., for example, Kirk-Othmer, "Encyclopedia of Chemical Technology", 1981, vol. 16, p. 402). These generally give ethylene homopolymers and copolymers having high molecular weights, but are relatively insensitive to hydrogen and thus do not allow the molecular weight to be controlled in a simple
 20 manner. In contrast, the use of bis(cyclopentadienyl)chromium (US 3,709,853), bis(indenyl)chromium or bis(fluorenyl)chromium (US 4,015,059) applied to an inorganic, oxidic support allows the molecular weight of polyethylene to be controlled in a simple manner by addition of hydrogen.

25 As in the case of Ziegler-Natta systems, catalyst systems having a uniquely defined, active center, known as single-site catalysts, have recently been sought in the case of the chromium compounds, too. Targeted variation of the ligand framework should enable activity, copolymerization behavior of the catalyst and the properties of polymers obtained in this way to be altered in a simple manner.

30 Thus, EP 0 742 046 claims constrained geometry complexes of transition group 6, a specific process for preparing them (via metal tetraamides) and a process for preparing a polyolefin in the presence of such catalysts. Polymerization examples are not given. The ligand framework comprises an anionic donor which is bound to a
 35 cyclopentadienyl radical.

In Organomet. 1996, 15, 5284-5286, K.H. Theopold et al. describe an analogous $\{[(\text{tert-butylamido})\text{dimethylsilyl}](\text{tetramethylcyclopentadienyl})\}$ chromium chloride complex for the polymerization of olefins. This complex selectively polymerizes

ethylene. Comonomers such as hexene are not incorporated, nor can propene be polymerized.

This disadvantage can be overcome by the use of structurally very similar systems. Thus, DE 197 10615 describes monocyclopentadienylchromium compounds substituted by donor ligands by means of which, for example, propene can also be polymerized. Here, the donor is from group 15 and is uncharged. The donor is bound to the cyclopentadienyl ring via a $(ZR_2)_n$ fragment, where R is hydrogen, alkyl or aryl, Z is an atom of group 14 and n is ≥ 1 . DE 196 30 580 specifically claims Z = carbon in combination with an amine donor.

WO 96/13529 describes reduced transition metal complexes of groups 4 to 6 of the Periodic Table with polydentate monoanionic ligands. These include cyclopentadienyl ligands containing a donor function. The examples are restricted to titanium compounds.

There are also ligand systems in which the donor group is rigidly joined to the cyclopentadienyl radical. Such ligand systems and their metal complexes are summarized by, for example, P. Jutzi and U. Siemeling in J. Organomet. Chem. (1995), 500, 175-185, section 3. In Chem. Ber. (1996), 129, 459-463, M. Enders et al. describe 8-quinolyl-substituted cyclopentadienyl ligands and their titanium trichloride and zirconium trichloride complexes. 2-Picolylcyclopentadienyltitanium trichloride in combination with MAO has been used by M. Blais, J. Chien and M. Rausch in Organomet. (1998), 17 (17) 3775-3783, for the polymerization of olefins.

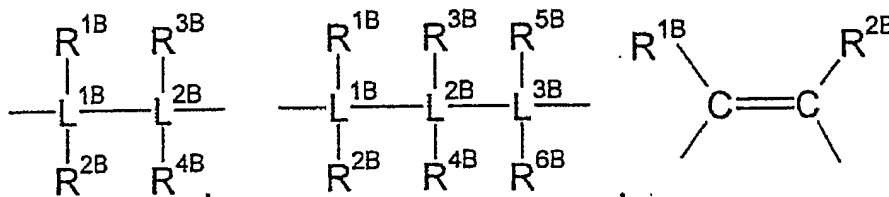
WO 01/12641 describes monocyclopentadienyl complexes of chromium, molybdenum and tungsten which bear, in particular, quinolyl or pyridyl donors which are bound either directly or via a C₁ or Si bridge to the cyclopentadienyl system.

It is an object of the present invention to find further transition metal complexes based on cyclopentadienyl ligands having a bridged donor which are suitable for the polymerization of olefins. A further object of the invention is to find an advantageous process for preparing such complexes.

We have found that the first of these objects is achieved by monocyclopentadienyl complexes which contain the structural feature of the formula $(Cp)(-Z-A)_mM(I)$, where the variables have the following meanings:

Cp is a cyclopentadienyl system,

Z is a bridge between A and Cp and is selected from the group consisting of



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where

$L^{1B}-L^{3B}$ are each, independently of one another, carbon or silicon,

10 $R^{1B}-R^{6B}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{7B}_3 , where the organic radicals $R^{1B}-R^{6B}$ may also be substituted by halogens and two geminal or vicinal radicals $R^{1B}-R^{6B}$ or a radical $R^{1B}-R^{6B}$ and A may also be joined to form a five- or six-membered ring and

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R^{7B} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{7B} may also be joined to form a five- or six-membered ring,

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A is an unsubstituted, substituted or fused, heteroaromatic ring system,

M is a metal selected from the group consisting of titanium in the oxidation state 3, vanadium, chromium, molybdenum and tungsten and

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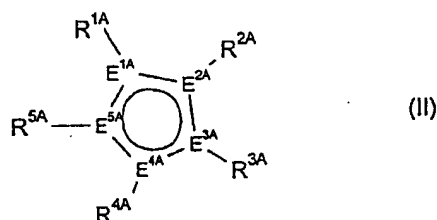
m is 1, 2 or 3.

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Furthermore, we have found a catalyst system comprising the monocyclopentadienyl complexes of the invention, the use of the monocyclopentadienyl complexes or of the catalyst system for the polymerization or copolymerization of olefins and a process for preparing polyolefins by polymerization or copolymerization of olefins in the presence of the monocyclopentadienyl complex or the catalyst system and polymers obtainable therefrom.

The monocyclopentadienyl complexes of the present invention contain the structural element of the formula $(Cp)(-Z-A)_mM$ (I), where the variables are as defined above. Further ligands can therefore be bound to the metal atom M. The number of further ligands depends, for example, on the oxidation state of the metal atom. Possible further ligands do not include further cyclopentadienyl systems. Suitable further ligands are monoanionic and dianionic ligands as are described, for example, for X. In addition, Lewis bases such as amines, ethers, ketones, aldehydes, esters, sulfides or phosphines can also be bound to the metal center M.

- 10 Cp is a cyclopentadienyl system which may be substituted as desired and/or fused with one or more aromatic, aliphatic, heterocyclic or heteroaromatic rings, wherein 1, 2 or 3 substituents, preferably 1 substituent, is the group -Z-A. The cyclopentadienyl skeleton itself is a C_5 -ring system having 6 π electrons, in which one of the carbon atoms can also be replaced by nitrogen or phosphorus, preferably phosphorus. Preference is given to using C_5 -ring systems without replacement by a heteroatom. A heteroaromatic ring containing at least one atom from the group consisting of N, P, O and S or an aromatic ring can, for example, be fused onto this cyclopentadienyl skeleton. In the present context, fused-on means that the heterocycle and the cyclopentadienyl skeleton have two atoms, preferably carbon atoms, in common.
- 20 Preference is given to cyclopentadienyl systems Cp of the formula (II)



where the variables have the following meanings:

- 25 $E^{1A}-E^{5A}$ are each carbon or not more than one E^{1A} to E^{5A} is phosphorus,
- $R^{1A}-R^{5A}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, NR^{6A}_2 , $N(SiR^{6A}_3)_2$, OR^{6A} , $OSiR^{6A}_3$, SiR^{6A}_3 , BR^{6A}_2 , where the organic radicals $R^{1A}-R^{5A}$ may also be substituted by halogens and two vicinal radicals $R^{1A}-R^{5A}$ may also be joined to form a five- or six-membered ring, and/or two vicinal radicals $R^{1A}-R^{5A}$ are joined to form a heterocycle which contains at least one atom from the group consisting of N, P, O and S,
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where 1, 2 or 3 substituents, preferably 1 substituent, R^{1A} - R^{5A} is a group -Z-A and

- R^{6A} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl radical and 6-20 carbon atoms in the aryl radical and two geminal radicals R^{6A} may also be joined to form a five- or six-membered ring.
- 10 In preferred cyclopentadienyl systems Cp, all E^{1A} to E^{5A} are carbon.
- Two vicinal radicals R^{1A} - R^{5A} can, in each case together with the E^{1A} - E^{5A} to which they are bound, form a heterocycle, preferably a heteroaromatic, which contains at least one atom from the group consisting of nitrogen, phosphorus, oxygen and sulfur, particularly preferably nitrogen and/or sulfur, with the E^{1A} - E^{5A} present in the heterocycle or heteroaromatic are preferably carbon atoms. Preference is given to heterocycles and heteroaromatics having a ring size of 5 or 6 ring atoms. Examples of 5-membered heterocycles, which may contain from 1 to 4 nitrogen atoms and/or a sulfur or oxygen atom as ring atoms in addition to carbon atoms, are 1,2-dihydro-furan, furan, thiophene, pyrrole, isoxazole, 3-isothiazole, pyrazole, oxazole, thiazole, imidazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-triazole and 1,2,4-triazole. Examples of 6-membered heteroaryl groups, which may contain from 1 to 4 nitrogen atoms and/or a phosphorus atom, are pyridine, phosphabenzene, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine and 1,2,3-triazine. The 5- and 6-membered heterocycles may also be substituted by C_1 - C_{10} -alkyl, C_6 - C_{10} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-10 carbon atoms in the aryl part, trialkylsilyl or halogens such as fluorine, chlorine or bromine, dialkylamide, alkylarylamide, diarylamide, alkoxy or aryloxy or be fused with one or more aromatics or heteroaromatics. Examples of the benzo-fused 5-membered heteroaryl groups are indole, indazole, benzofuran, benzothiophene, benzothiazole, benzoxazole and benzimidazole. Examples of benzo-fused 6-membered heteroaryl groups are chroman, benzopyran, quinoline, isoquinoline, cinnoline, phthalazine, quinazoline, quinoxaline, 1,10-phenanthroline and quinolizine. Naming and numbering of the heterocycles has been taken from Lettau, Chemie der Heterocyclen, 1st edition, VEB, Weinheim 1979.
- 35 The heterocycles/heteroaromatics are preferably fused with the cyclopentadienyl skeleton via a C-C double bond of the heterocycle/heteroaromatic. Heterocycles/heteroaromatics containing a heteroatom are preferably 2,3-fused or b-fused.

Examples of cyclopentadienyl systems Cp having a fused heterocycle are thiapentalene, 2-methylthiapentalene, 2-ethylthiapentalene, 2-isopropylthiapentalene, 2-n-butylthiapentalene, 2-tert-butylthiapentalene, 2-trimethylsilylthiapentalene, 2-phenylthiapentalene, 2-naphthylthiapentalene, 3-methylthiopentalene, 4-phenyl-2,6-dimethyl-1-thiapentalene, 4-phenyl-2,6-diethyl-1-thiapentalene, 4-phenyl-2,6-diisopropyl-1-thiapentalene, 4-phenyl-2,6-di-n-butyl-1-thiapentalene, 4-phenyl-2,6-di(trimethylsilyl)-1-thiapentalene, azapentalene, 2-methylazapentalene, 2-ethylazapentalene, 2-isopropylazapentalene, 2-n-butylazapentalene, 2-trimethylsilylazapentalene, 2-phenylazapentalene, 2-naphthylazapentalene, 1-phenyl-2,5-dimethyl-1-azapentalene, 1-phenyl-2,5-diethyl-1-azapentalene, 1-phenyl-2,5-di-n-butyl-1-azapentalene, 1-phenyl-2,5-di-tert-butyl-1-azapentalene, 1-phenyl-2,5-di(trimethylsilyl)-1-azapentalene, 1-tert-butyl-2,5-dimethyl-1-azapentalene, oxapentalene, phosphapentalene, 1-phenyl-2,5-dimethyl-1-phosphapentalene, 1-phenyl-2,5-diethyl-1-phosphapentalene, 1-phenyl-2,5-di-n-butyl-1-phosphapentalene, 1-phenyl-2,5-di-tert-butyl-1-phosphapentalene, 1-phenyl-2,5-di(trimethylsilyl)-1-phosphapentalene, 1-methyl-2,5-dimethyl-1-phosphapentalene, 1-tert-butyl-2,5-dimethyl-1-phosphapentalene, 7-cyclopenta[1,2]thieno[3,4]cyclopentadiene or 7-cyclopenta[1,2]pyrrolo[3,4]cyclopentadiene.

In further preferred cyclopentadienyl systems Cp, four of the radicals R^{1A} - R^{5A} , i.e. two pairs of vicinal radicals, form two heterocycles, in particular heteroaromatics. The heterocyclic systems are the same as those described in more detail above. Examples of cyclopentadienyl systems Cp having two fused-on heterocycles are 7-cyclopentadithiophene, 7-cyclopentadipyrrole or 7-cyclopentadiphosphole.

The synthesis of such cyclopentadienyl systems having a fused-on heterocycle is described, for example, in the abovementioned WO 98/22486. In "metalorganic catalysts for synthesis and polymerization", Springer Verlag 1999, p. 150 ff, Ewen et al. describe further syntheses of these cyclopentadienyl systems.

The polymerization behavior of the metal complexes can likewise be influenced by variation of the substituents R^{1A} - R^{5A} . The number and type of substituents can influence the ability of the olefins to be polymerized to gain access to the metal atom M. This makes it possible to modify the activity and selectivity of the catalyst in respect of various monomers, in particular bulky monomers. Since the substituents can also influence the rate of termination reactions of the growing polymer chain, the molecular weight of the polymers formed can also be altered in this way. The chemical structure of the substituents R^{1A} to R^{5A} can therefore be varied within a wide range in order to achieve the desired results and to obtain a tailored catalyst system.

Possible carboorganic substituents R^{1A} - R^{5A} are, for example, the following:

- C_1 - C_{20} -alkyl which may be linear or branched, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl or n-dodecyl, 5- to 7-membered cycloalkyl which may in turn bear a C_6 - C_{10} -aryl group as substituent, e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclododecyl, C_2 - C_{20} -alkenyl which may be linear, cyclic or branched and have an internal or terminal double bond, e.g. vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl, C_6 - C_{20} -aryl which may be substituted by further alkyl groups, e.g. phenyl, naphthyl, biphenyl, anthranyl, o-, m-, p-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, or arylalkyl which may be substituted by further alkyl groups, e.g. benzyl, o-, m-, p-methylbenzyl, 1- or 2-ethylphenyl, where two R^{1A} to R^{5A} may also be joined to form a 5- or 6-membered ring and the organic radicals R^{1A} - R^{5A} may also be substituted by halogens, e.g. fluorine, chlorine or bromine. Furthermore, R^{1A} - R^{5A} can also be amino or alkoxyl, for example dimethylamino, n-pyrrolidinyl, picolinyl, methoxy, ethoxy or isopropoxy. In organosilicon substituents SiR^{6A}_3 , R^{6A} may be the same radicals as described in more detail above for R^{1A} - R^{5A} , with two R^{6A} also being able to be joined to form a 5- or 6-membered ring. Examples of substituents SiR^{6A}_3 are trimethylsilyl, triethylsilyl, butyldimethylsilyl, tributylsilyl, tri-tert-butylsilyl, triallylsilyl, triphenylsilyl and dimethylphenylsilyl. These SiR^{6A}_3 radicals can also be joined to the cyclopentadienyl skeleton via an oxygen or nitrogen atom, for example trimethylsilyloxy, triethylsilyloxy, butyldimethylsilyloxy, tributylsilyloxy or tri-tert-butylsilyloxy. Preferred radicals R^{1A} - R^{5A} are hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, vinyl, allyl, benzyl, phenyl, ortho-dialkyl- or ortho-dichloro-substituted phenyls, trialkyl- or trichloro-substituted phenyls, naphthyl, biphenyl and anthranyl. As organosilicon substituents, particular preference is given to trialkylsilyl groups having from 1 to 10 carbon atoms in the alkyl radical, in particular trimethylsilyl groups.

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- Examples of such cyclopentadienyl systems (without the group -Z-A, which is preferably located in the 1 position) are 3-methylcyclopentadienyl, 3-ethylcyclopentadienyl, 3-isopropylcyclopentadienyl, 3-tert-butylcyclopentadienyl, dialkylcyclopentadienyl such as tetrahydroindenyl, 2,4-dimethylcyclopentadienyl or 3-methyl-5-tert-butylcyclopentadienyl, trialkylcyclopentadienyl such as 2,3,5-trimethylcyclopentadienyl or tetraalkylcyclopentadienyl such as 2,3,4,5-tetramethylcyclopentadienyl.

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Preference is also given to compounds in which two vicinal radicals R^{1A} - R^{5A} form a

cyclic fused ring system, i.e. together with the $E^{1A}-E^{5A}$ skeleton, preferably a C_5 -cyclopentadienyl skeleton, form, for example, an unsubstituted or substituted indenyl, benzindenyl, phenanthrenyl, fluorenyl or tetrahydroindenyl system, for example indenyl, 2-methylindenyl, 2-ethylindenyl, 2-isopropylindenyl, 3-methyl-
 5 indenyl, benzindenyl or 2-methylbenzindenyl.

The fused ring system may be a further C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, NR^{6A}_2 , $N(SiR^{6A}_3)_2$, OR^{6A} , $OSiR^{6A}_3$ or SiR^{6A}_3 groups, e.g. 4-methyl-
 10 indenyl, 4-ethylindenyl, 4-isopropylindenyl, 5-methylindenyl, 4-phenylindenyl, 5-methyl-4-phenylindenyl, 2-methyl-4-phenylindenyl or 4-naphthylindenyl.

Preferred substituents $R^{1A}-R^{5A}$ which do not form -Z-A are the carboorganic substituents described above and the carboorganic substituents which form a cyclic
 15 fused ring system, in particular their preferred embodiments.

m can be 1, 2 or 3, i.e. 1, 2 or 3 radicals $R^{1A}-R^{5A}$ are -Z-A, where if 2 or 3 -Z-A radicals are present, these can be identical or different. Preference is given to only one of the radicals $R^{1A}-R^{5A}$ being -Z-A ($m = 1$).

20 As in the case of the metallocenes, the monocyclopentadienyl complexes of the present invention may be chiral. Thus, one of the substituents $R^{1A}-R^{5A}$ of the cyclopentadienyl skeleton can have one or more chiral centers, or else the cyclopentadienyl system Cp can itself be enantiotopic, so that chirality is induced only when the cyclopentadienyl system is bound to the transition metal M (for formalisms regarding
 25 chirality in cyclopentadienyl compounds, cf. R. Halterman, Chem. Rev. 92, (1992), 965-994).

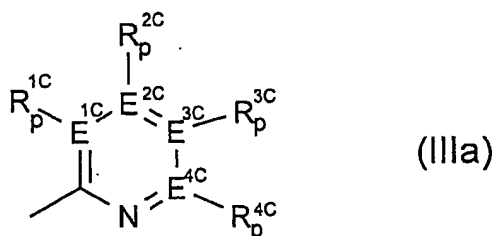
Possible carboorganic substituents $R^{1B}-R^{6B}$ on the link Z are, for example, the following: C_1 - C_{20} -alkyl which may be linear or branched, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl or n-dodecyl, 5- to 7-membered cycloalkyl which may in turn bear a
 30 C_6 - C_{10} -aryl group as substituent, e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclododecyl, C_2 - C_{20} -alkenyl which
 35 may be linear, cyclic or branched and have an internal or terminal double bond, e.g. vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl, C_6 - C_{20} -aryl which may be substituted by further alkyl groups, e.g. phenyl, naphthyl, biphenyl, anthranyl, o-, m-, p-methylphenyl, 2,3-,

- 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, or arylalkyl which may be substituted by further alkyl groups, e.g. benzyl, o-, m-, p-methylbenzyl, 1- or 2-ethylphenyl, where two R^{1B} to R^{6B} may also be joined to form a 5- or 6-membered ring for example cyclohexane, and the organic radicals
- 5 R^{1B} - R^{6B} may also be substituted by halogens, e.g. fluorine, chlorine or bromine, and alkyl or aryl. In organosilicon substituents SiR^{7B}_3 , R^{7B} may be the same radicals as described in more detail above for R^{1B} - R^{6B} , with two R^{7B} also being able to be joined to form a 5- or 6-membered ring. Examples of substituents SiR^{7B}_3 are trimethylsilyl, triethylsilyl, butyldimethylsilyl, tributylsilyl, tri-tert-butylsilyl, triallylsilyl, triphenyl-
- 10 silyl and dimethylphenylsilyl. Preferred radicals R^{1B} - R^{6B} are hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, benzyl, phenyl, ortho-dialkyl- or ortho-dichloro-substituted phenyls, trialkyl- or trichloro-substituted phenyl, naphthyl, biphenyl and anthranyl.
- 15 The bridge Z between the cyclopentadienyl system Cp and the heterocycle A is an organic, preferably divalent bridge comprising carbon and/or silicon units. Z can be bound to the cyclopentadienyl skeleton or to the heterocycle or the fused-on ring of the cyclopentadienyl system. Z is preferably bound to the cyclopentadienyl skeleton. A change in the length of the link between the cyclopentadienyl system and A can
- 20 influence the activity of the catalyst. Very particular preference is given to Z being bound to the cyclopentadienyl skeleton in a position adjacent to the fused-on heterocycle or aromatic. Thus, for example, if the heterocycle or aromatic is fused-on in the 2,3 position of the cyclopentadienyl skeleton, Z is preferably located in the 1 or 4 position of the cyclopentadienyl skeleton.
- 25 Preferred bridges Z are $-C(R^{1B}R^{2B})-C(R^{3B}R^{4B})-$, $-C(R^{1B}R^{2B})-Si(R^{3B}R^{4B})-$ or 1,2-phenylene. The $-C(R^{1B}R^{2B})$ group in $-C(R^{1B}R^{2B})-Si(R^{3B}R^{4B})$ can be bound to A or Cp. $-C(R^{1B}R^{2B})-$ is preferably bound to A, since these compounds are simple and inexpensive to prepare. In these, $-C(R^{1B}R^{2B})-$ is preferably CH_2 , so that $-CH_2-C(R^{3B}R^{4B})-$ and
- 30 $CH_2-Si(R^{3B}R^{4B})-$ are particularly preferred as bridges Z, preferably $-CH_2-C(CH_3)_2-$. The CH_2 group in these, i.e. $-CH_2-C(CH_3)_2-$, is preferably bound to A. Z is particularly preferably a $-C(R^{1B}R^{2B})-Si(R^{3B}R^{4B})-$, 1,2-cyclohexanediyl or 1,2-phenylene bridge. The above-described embodiments and preferred embodiments for R^{1B} - R^{4B} and R^{7B} also apply to these preferred monocyclopentadienyl complexes.
- 35 A is an unsubstituted, substituted or fused heteroaromatic ring system whose ring can contain, in addition to carbon atoms, heteroatoms selected from the group consisting of oxygen, sulfur, nitrogen and phosphorus. Examples of 5-membered heteroaryl

groups, which can contain from 1 to 4 nitrogen atoms or from 1 to 3 nitrogen atoms and/or a sulfur or oxygen atom as ring atoms in addition to carbon, are 2-furyl, 2-thienyl, 2-pyrrolyl, 3-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 5-isothiazolyl, 1-pyrazolyl, 3-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,3,4-oxadiazol-2-yl and 1,2,4-triazol-3-yl. Examples of 6-membered heteroaryl groups, which can contain from 1 to 4 nitrogen atoms and/or a phosphorus atom, are 2-pyridinyl, 2-phosphabenzene, 3-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-1-yl and 1,2,4-triazin-3-yl, 1,2,4-triazin-5-yl and 1,2,4-triazin-6-yl. The 5-membered and 6-membered heteroaryl groups can also be substituted by C₁-C₁₀-alkyl, C₆-C₁₀-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-10 carbon atoms in the aryl part, trialkylsilyl or halogens such as fluorine, chlorine or bromine or be fused with one or more aromatics or heteroaromatics. Examples of benzo-fused 5-membered heteroaryl groups are 2-indolyl, 7-indolyl, 2-coumaronyl, 7-coumaronyl, 2-thianaphthenyl, 7-thianaphthenyl, 3-indazolyl, 7-indazolyl, 2-benzimidazolyl and 7-benzimidazolyl. Examples of benzo-fused 6-membered heteroaryl groups are 2-quinolyl, 8-quinolyl, 3-cinnolyl, 8-cinnolyl, 1-phthalazyl, 2-quinazolyl, 4-quinazolyl, 8-quinazolyl, 5-quinoxalyl, 4-acridyl, 1-phenanthridyl and 1-phenazyl.

A can bind to the metal M either intermolecularly or intramolecularly. A is preferably bound intramolecularly to M. The synthesis to bind A to the cyclopentadienyl ring can be carried out, for example, by a method analogous to that of M. Enders et al. in Chem. Ber. (1996), 129, 459-463 or P. Jutzi and U. Siemeling in J. Orgmet. Chem. (1995), 500, 175-185.

Among these heteroaromatic systems, particular preference is given to unsubstituted, substituted and/or fused 6-membered heteroaromatics having 1, 2, 3, 4 or 5 nitrogen atoms in the heteroaromatic unit bound to Z, in particular 2-pyridyl or 2-quinolyl. A is therefore preferably a group of the formula (IIIa)

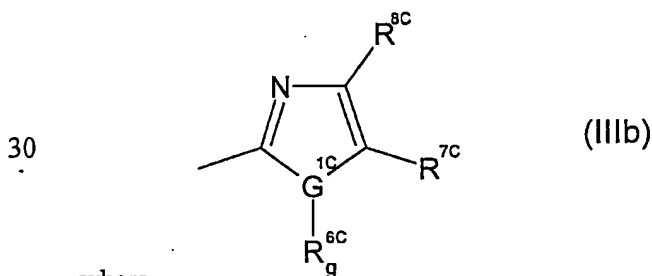


where
 $\text{E}^{1C} - \text{E}^{4C}$ are each carbon or nitrogen,

- $R^{1C}-R^{4C}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{5C}_3 , where the organic radicals $R^{1C}-R^{4C}$ may also be substituted by halogens or nitrogen and further C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{5C}_3 groups and two vicinal radicals $R^{1C}-R^{4C}$ or R^{1C} and Z may also be joined to form a 5- or 6-membered ring and
- R^{5C} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{5C} may also be joined to form a five- or six-membered ring and
- p is 0 when $E^{1C}-E^{4C}$ is nitrogen and 1 when $E^{1C}-E^{4C}$ is carbon.

In particular, 0 or 1 $E^{1C}-E^{4C}$ is nitrogen and the others are carbon. A is particularly preferably 2-pyridyl, 6-methyl-2-pyridyl, 4-methyl-2-pyridyl, 5-methyl-2-pyridyl, 5-ethyl-2-pyridyl, 4,6-dimethyl-2-pyridyl, 3-pyridazyl, 4-pyrimidyl, 6-methyl-4-pyrimidyl, 2-pyrazinyl, 6-methyl-2-pyrazinyl, 5-methyl-2-pyrazinyl, 3-methyl-2-pyrazinyl, 3-ethylpyrazinyl, 3,5,6-trimethyl-2-pyrazinyl, 2-quinolyl, 4-methyl-2-quinolyl, 4-methyl-2-quinolyl, 6-methyl-2-quinolyl, 7-methyl-2-quinolyl, 2-quinoxalyl or 3-methyl-2-quinoxalyl.

In another preferred embodiment A is a group of the formula (IIIb)



where G^{1C} is nitrogen, phosphorus, sulfur or oxygen,

- $R^{6C}-R^{8C}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{9C}_3 , where

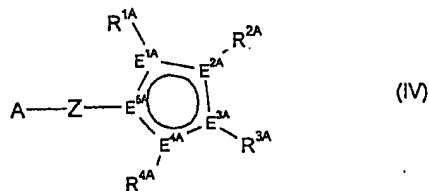
the organic radicals $R^{6C}-R^{8C}$ may also be substituted by halogens or nitrogen and further C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{9C}_3 groups and two vincinal radicals $R^{6C}-R^{8C}$ or R^{6C} and Z may also be joined to form a 5- or 6-membered ring and

R^{9C} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{9C} may also be joined to form a five- or six-membered ring and

g is 0 when G^{1C} is sulfur or oxygen and 1 when G^{1C} is nitrogen or phosphorus.

15 Preferably G^{1C} is nitrogen. A is particularly preferably 2-(1,3-oxazolyl), 2-(benzoxazolyl), 2-(1,3-thiazolyl), 2-(benzothiazolyl), 2-imidazolyl, 2-(1-methyl-imidazolyl), 2-(1-butyl-imidazolyl), 2-(1-benzyl-imidazolyl), 2-(1-phenyl-imidazolyl) or 2-benzimidazolyl.

20 In preferred monocyclopentadienyl complexes, the cyclopentadienyl system Cp and -Z-A form a ligand (Cp-Z-A) of formula IV:



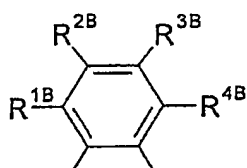
where the variables A, Z, E^{1A} to E^{5A} and R^{6A} are as defined above and their preferred embodiments are also preferred here and

25 $R^{1A}-R^{4A}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, NR^{6A}_2 , $N(SiR^{6A}_3)_2$, OR^{6A} , $OSiR^{6A}_3$, SiR^{6A}_3 , BR^{6A}_2 , where the organic radicals $R^{1A}-R^{4A}$ may also be substituted by halogens and two vicinal radicals $R^{1A}-R^{4A}$ may also be joined to form a five- or six-membered ring, and/or two vicinal radicals $R^{1A}-R^{4A}$ are joined to form a heterocycle which contains at least one atom from the group consisting of N, P, O and S.

35 For $R^{1A}-R^{4A}$, what has been said above and the preferred embodiments likewise apply.

In particular, the monocyclopentadienyl complex contains the ligand (Cp-Z-A) of the formula IV in the following preferred embodiment:

Z is selected from among $-C(R^{1B}R^{2B})-Si(R^{3B}R^{4B})-$, $-CH_2-C(R^{3B}R^{4B})-$ and 1,2-phenylene, preferably $-CH_2-C(R^{3B}R^{4B})-$, where $-C(R^{1B}R^{2B})-$ and $-CH_2-$ is preferably bound to A and the phenylene can be substituted further:



where

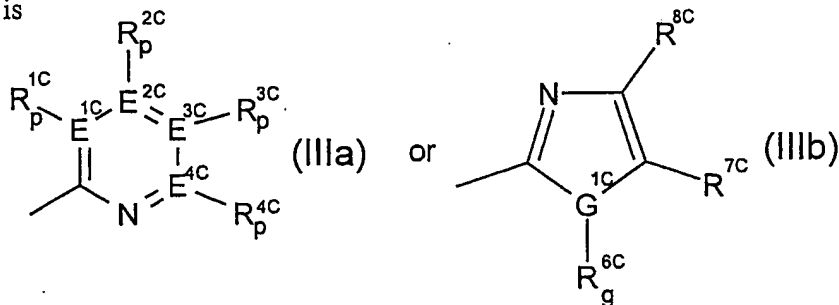
$R^{1B}-R^{2B}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{7B}_3 , where the organic radicals $R^{1B}-R^{2B}$ may also be substituted by halogens and two geminal or vicinal radicals $R^{1B}-R^{4B}$ may also be joined to form a five- or six-membered ring and

$R^{3B}-R^{4B}$ are each, independently of one another, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{7B}_3 , where the organic radicals $R^{3B}-R^{4B}$ may also be substituted by halogens and two geminal or vicinal radicals $R^{1B}-R^{4B}$ may also be joined to form a five- or six-membered ring and

R^{7B} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{7B} may also be joined to form a five- or six-membered ring and

A

is



where

$E^{1C}-E^{4C}$ are each carbon or nitrogen,

5 $R^{1C}-R^{4C}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{5C}_3 , where the organic radicals $R^{1C}-R^{4C}$ may also be substituted by halogens and further C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1
10 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{5C}_3 groups and two vincinal radicals $R^{1C}-R^{4C}$ or R^{1C} and Z may also be joined to form a 5- or 6-membered ring and

R^{5C} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl,
15 C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{5C} may also be joined to form a five- or six-membered ring and

p is 0 when $E^{1C}-E^{4C}$ is nitrogen and 1 when $E^{1C}-E^{4C}$ is carbon and

20 G^{1C} is nitrogen, phosphorus, sulfur or oxygen,

$R^{6C}-R^{8C}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl,
25 C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{9C}_3 , where the organic radicals $R^{6C}-R^{8C}$ may also be substituted by halogens or nitrogen and further C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{9C}_3 groups and two vincinal radicals $R^{6C}-R^{8C}$ or R^{6C}
30 and Z may also be joined to form a 5- or 6-membered ring and

R^{9C} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl,
35 C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{9C} may also be joined to form a five- or six-membered ring and

g is 0 when G^{1C} is sulfur or oxygen and 1 when G^{1C} is nitrogen or phosphorus.

For A, Z, R^{1A} - R^{4A} , R^{6A} , R^{1B} - R^{4B} and R^{7B} what has been said above and the preferred embodiments likewise apply.

- 5 M is a metal selected from the group consisting of titanium in the oxidation state 3, vanadium, chromium, molybdenum and tungsten, preferably titanium in the oxidation state 3, chromium, molybdenum and tungsten. Particular preference is given to chromium in the oxidation states 2, 3 and 4, in particular 3. The metal complexes, in particular the chromium complexes, can be obtained in simple manner by reacting the
10 corresponding metal salts, e.g. metal chlorides, with the ligand anion (e.g. using methods analogous to the examples in DE 197 10615.

Among the monocyclopentadienyl complexes of the present invention, preference is given to those of the formula $(Cp)(-Z-A)_mMX_k(V)$, where the variables Cp, Z, A, m
15 and M are as defined above and their preferred embodiments are also preferred here and:

- X are each, independently of one another, fluorine, chlorine, bromine, iodine, hydrogen, C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_6 - C_{20} -aryl, alkylaryl
20 having 1-10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, NR^1R^2 , OR^1 , SR^1 , SO_3R^1 , $OC(O)R^1$, CN, SCN, β -diketonate, CO, BF_4^- , PF_6^- or a bulky noncoordinating anion,
- R^1 - R^2 are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms
25 in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^3_3 , where the organic radicals R^1 - R^2 may also be substituted by halogens or nitrogen- and oxygen-containing groups and two radicals R^1 - R^2 may also be joined to form a 5- or 6-membered ring,
- R^3 are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms
30 in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^3 may also be joined to form a 5- or 6-membered ring and
- 35 k is 1, 2 or 3.

The embodiments and preferred embodiments of Cp, Z, A, m and M described above

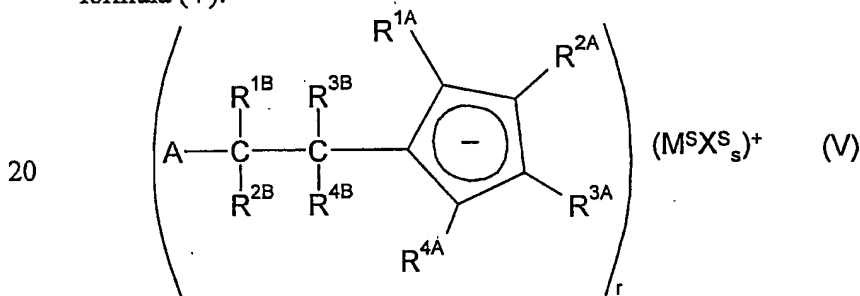
also apply individually and in combination to these preferred monocyclopentadienyl complexes.

The ligands X can result, for example, from the choice of the corresponding starting metal compounds which are used for the synthesis of the monocyclopentadienyl complexes, but can also be varied afterwards. Suitable ligands X are, in particular, the halogens fluorine, chlorine, bromine or iodine, in particular chlorine. Alkyl radicals such as methyl, ethyl, propyl, butyl, vinyl, allyl, phenyl or benzyl are also advantageous ligands X. Further possible ligands X are, purely by way of example and not in any way exhaustively, trifluoroacetate, BF_4^- , PF_6^- and weakly coordinating or noncoordinating anions (cf., for example, Strauss in Chem. Rev. 1993, 93, 927-942) such as $\text{B}(\text{C}_6\text{F}_5)_4^-$.

Amides, alkoxides, sulfonates, carboxylates and β -diketonates are also particularly suitable ligands X. Variation of the radicals R^1 and R^2 enables, for example, physical properties such as solubility to be finely adjusted. Possible carboorganic substituents R^1 - R^2 are, for example, the following: C_1 - C_{20} -alkyl which may be linear or branched, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl or n-dodecyl, 5- to 7-membered cycloalkyl which may in turn bear a C_6 - C_{10} -aryl group as substituent, e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclododecyl, C_2 - C_{20} -alkenyl which may be linear, cyclic or branched and have an internal or terminal double bond, e.g. vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl, C_6 - C_{20} -aryl which may be substituted by further alkyl groups and/or N- or O-containing radicals, e.g. phenyl, naphthyl, biphenyl, anthranyl, o-, m-, p-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, 2-methoxyphenyl, 2-N,N-dimethylaminophenyl or arylalkyl which may be substituted by further alkyl groups, e.g. benzyl, o-, m-, p-methylbenzyl, 1- or 2-ethylphenyl, where R^1 may also be joined to R^2 to form a 5- or 6-membered ring and the organic radicals R^1 - R^2 may also be substituted by halogens, e.g. fluorine, chlorine or bromine. In organosilicon substituents SiR^3_3 , R^3 may be the same radicals as described in more detail above for R^1 - R^2 , with two R^3 also being able to be joined to form a 5- or 6-membered ring. Examples of substituents SiR^3_3 are trimethylsilyl, triethylsilyl, butyldimethylsilyl, tributylsilyl, triallylsilyl, triphenylsilyl and dimethylphenylsilyl. Preference is given to using C_1 - C_{10} -alkyl such as methyl, ethyl, n-propyl, n-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl and also vinyl, allyl, benzyl and phenyl as radicals R^1 and R^2 . Some of these substituted ligands X are very particularly preferably used since they are obtainable from cheap and readily available starting materials. In a

particularly preferred embodiment X is dimethylamide, methoxide, ethoxide, isopropoxide, phenoxide, naphthoxide, triflate, p-toluenesulfonate, acetate, or acetylacetonate

- 5 The number k of the ligands X depends on the oxidation state of the transition metal M. The number k can therefore not be specified in general terms. The oxidation state of the transition metals M in catalytically active complexes is usually known to a person skilled in the art. Chromium, molybdenum and tungsten are very probably present in the oxidation state +3, vanadium in the oxidation state +3 or +4. However,
 10 it is also possible to use complexes whose oxidation state does not correspond to that of the active catalyst. Such complexes can then be appropriately reduced or oxidized by means of suitable activators. Preference is given to using chromium complexes in the oxidation state +3 and titanium complexes in the oxidation state 3.
- 15 Furthermore, we have found a process for preparing cyclopentadienyl systems of the formula (V):

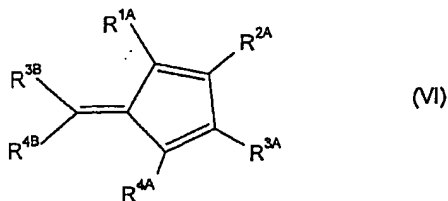


where the variables have the following meanings:

- 25 $\text{R}^{1\text{A}}-\text{R}^{4\text{A}}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, $\text{NR}^{6\text{A}}_2$, $\text{N}(\text{SiR}^{6\text{A}}_3)_2$, $\text{OR}^{6\text{A}}$, $\text{OSiR}^{6\text{A}}_3$, $\text{SiR}^{6\text{A}}_3$, where the organic radicals $\text{R}^{1\text{A}}-\text{R}^{4\text{A}}$
 30 may also be substituted by halogens and two vicinal radicals $\text{R}^{1\text{A}}-\text{R}^{4\text{A}}$ may also be joined to form a five- or six-membered ring, and/or two vicinal radicals $\text{R}^{1\text{A}}-\text{R}^{4\text{A}}$ are joined to form a heterocycle which contains at least one atom from the group consisting of N, P, O and S.
- 35 $\text{R}^{6\text{A}}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two geminal radicals $\text{R}^{6\text{A}}$ may also be joined to form a five- or six-membered ring,

- A is an unsubstituted, substituted or fused, heteroaromatic ring system,
- $R^{1B}-R^{4B}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{7B}_3 , where the organic radicals $R^{1B}-R^{4B}$ may also be substituted by halogens and two geminal vicinal radicals $R^{1B}-R^{4B}$ may also be joined to form a five- or six-membered ring and
- R^{7B} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{7B} may also be joined to form a five- or six-membered ring,
- M^S a metal of group 1, 2 or 3 of the Periodic Table of the Elements,
- X^S are each, independently of one another, fluorine, chlorine, bromine, iodine, hydrogen, C_1-C_{10} -alkyl, C_2-C_{10} -alkenyl, C_6-C_{20} -aryl, alkylaryl having 1-10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, NR^1R^2 , OR^1 , SR^1 , SO_3R^1 , $OC(O)R^1$, CN, SCN, β -diketonate, CO, BF_4^- , PF_6^- or a bulky noncoordinating anion and
- s 0, 1 or 2,
- r 1 or 2, with the proviso that $s + r$ is the oxidation state of $M^S - 1$,

which comprises reacting $(A-CR^{1B}R^{2B-})_r(M^S X^S_s)^+$ with a fulvene of the formula (VI)



where the variables are as defined above.

The variables and their preferred embodiments have already been described above. Fulvenes have been known for a long time and can be prepared, for example, by the method of Freiesleben, *Angew. Chem.* 75 (1963), p. 576.

The X^S ligands provide the negative charge to an overall neutral cyclopentadienyl system (V) and are preferably halogens, i.e. chlorine and bromine. The counterion $M^S X^S_s$ of the cyclopentadienyl system anion in formula (V) is the cation of the
 5 A- $CR^{1B}R^{2B-}$ anion. M^S is generally a metal of group 1, 2 or 3 of the Periodic Table of the Elements, which bears s X^S ligands, so that the formal oxidation state of M^S minus s equals -1 . M^S may bear further neutral ligands. Particular preference is given to M^S being lithium, sodium or potassium cations which may also bear uncharged ligands such as amines or ethers and s is 0 and r is 1. Particular preference is also given to M^S
 10 being magnesium and s is 1 and r is 1, e.i. $M^S X^S_s$ being magnesium chloride or magnesium bromide cations which may likewise bear further uncharged ligands.

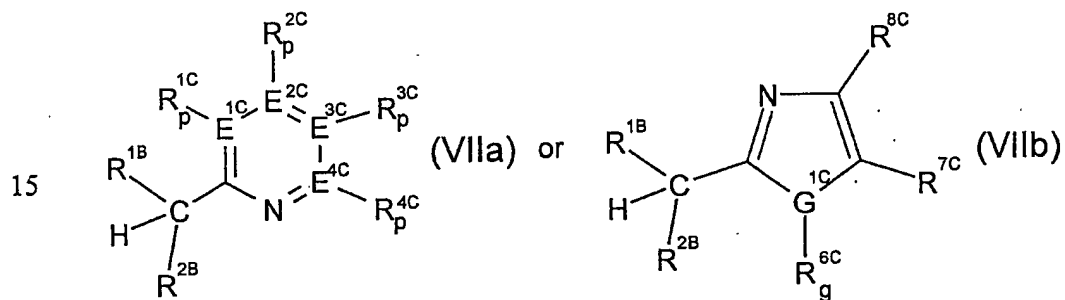
The A- $CR^{1B}R^{2B-}$ anion is usually obtained by deprotonation of A- $CR^{1B}R^{2B}H$. Strong bases such as lithium alkyls, sodium hydride, sodium amides, sodium alkoxides,
 15 sodium alkyls, potassium hydride, potassium amides, potassium alkoxides, potassium alkyls, magnesium alkyls, alkylmagnesium halides or mixtures thereof can be used for this purpose. The molar ratio of base to A- $CR^{1B}R^{2B}H$ is usually in the range from 0.4:1 to 100:1, preferably in the range from 0.9:1 to 10:1 and particularly preferably from 0.95:1 to 1.1:1. Examples of such deprotonations are described in L. Brandsma,
 20 Preparative polar organometallic chemistry 2, pp. 133-142.

As solvent for the deprotonation, it is possible to use all aprotic solvents, in particular aliphatic and aromatic hydrocarbons such as n-pentane, n-hexane, isohexane, n-heptane, isooheptane, decalin, benzene, toluene, ethylbenzene or xylene or ethers such as
 25 diethyl ether, dibutyl ether, tetrahydrofuran, dimethoxyethane or diethylene glycol dimethyl ether and mixtures thereof. The deprotonation can be carried out at from -100 to $+160^\circ C$, in particular from -80 to $100^\circ C$. At temperatures above $40^\circ C$, preference is given to using aromatic or aliphatic solvents which contain no ethers or only small proportions of ethers.

30 The unsubstituted, substituted or fused, heteroaromatic ring system A has the same meanings as described above and bears a $CR^{1B}R^{2B}H$ group. Preferably A is of the formula IIIa or IIIb with the $CR^{1B}R^{2B}H$ group in place where Z is located. The radicals R^{1B} and R^{2B} and their preferred embodiments have likewise already been
 35 described above and is particularly preferable hydrogen. This group is preferably located in the ortho position relative to a heteroatom of A, in particular a nitrogen atom if one is present in A. A- $CR^{1B}R^{2B}H$ is preferably 2-methylfuran, 2,5-dimethylfuran, 2-ethylfuran, 1,2-dimethylpyrrole, 1,2,3-trimethylpyrrole, 1,3-dimethylpyra-

zole, 1,2-dimethylimidazole, 1-decyl-2-methylimidazole, 1-methyl-2-undecylimidazole, 2-picoline, 2-ethylpyridine, 2-propylpyridine, 2-benzylpyridine, 2,6-lutidine, 2,4-lutidine, 2,5-lutidine, 2,3-cycloheptenopyridine, 5-ethyl-2-methylpyridine, 2,4,6-collidine, 3-methylpyridazine, 4-methylpyrimidine, 4,6-dimethylpyrimidine, 2-methylpyrazine, 2-ethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, 2,3-dimethylpyrazine, 2,3-diethylpyrazine, tetrahydroquinoxaline, tetramethylpyrazine, quinaldine, 2,4-dimethylquinoline, 2,6-dimethylquinoline, 2,7-dimethylquinoline, 2-methylquinoxaline, 2,3-dimethylquinoxaline or neocuproin.

A-CR^{1B}R^{2B}H is particularly preferably a group of the formula (VIIa) or (VIIb)



where the variables have the following meanings:

20

E^{1C}-E^{4C} are each carbon or nitrogen,

25

R^{1C}-R^{4C} are each, independently of one another, hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{5C}₃, where the organic radicals R^{1C}-R^{4C} may also be substituted by halogens or nitrogen and further C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, alkyl aryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{5C}₃ groups and two vicinal radicals R^{1C}-R^{4C} or R^{1C} and R^{1B} may also be joined to form a five- or six-membered ring, and

30

R^{5C} are each, independently of one another, hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{5C} may also be joined to form a five- or six-membered ring,

35

p is 0 when E^{1C}-E^{4C} is nitrogen and 1 when E^{1C}-E^{4C} is carbon,

p

- G^{1C} is nitrogen, phosphorus, sulfur or oxygen,
- $R^{6C}-R^{8C}$ are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{9C}_3 , where the organic radicals $R^{6C}-R^{8C}$ may also be substituted by halogens or nitrogen and further C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{9C}_3 groups and two vincinal radicals $R^{6C}-R^{8C}$ or R^{6C} and Z may also be joined to form a 5- or 6-membered ring and
- R^{9C} are each, independently of one another, hydrogen, C_1-C_{20} -alkyl, C_2-C_{20} -alkenyl, C_6-C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{9C} may also be joined to form a five- or six-membered ring and
- g is 0 when G^{1C} is sulfur or oxygen and 1 when G^{1C} is nitrogen or phosphorus.
- 20 In particular, 0 or 1 $E^{1C}-E^{4C}$ is nitrogen and the others are carbon. Particularly preferred $A-CR^{1B}R^{2B}H$ systems of formula VIIa are 2-picoline, 2-ethylpyridine, 2-propylpyridine, 2-benzylpyridine, 2,6-lutidine, 2,4-lutidine, 2,5-lutidine, 2,3-cycloheptenopyridine, 5-ethyl-2-methylpyridine, 2,4,6-collidine, 3-methylpyridazine, 4-methylpyrimidine, 4,6-dimethylpyrimidine, 2-methylpyrazine, 2-ethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, 2,3-dimethylpyrazine, 2,3-diethylpyrazine, tetrahydroquinoxaline, tetramethylpyrazine, quinaldine, 2,4-dimethylquinoline, 2,6-dimethylquinoline, 2,7-dimethylquinoline, 2-methylquinoxaline, 2,3-dimethylquinoxaline or neocuproin.
- 30 Preferably G^{1C} is nitrogen. Particularly preferred $A-CR^{1B}R^{2B}H$ systems of formula VIIb are 2-methyl-(1,3-oxazolyl), 2-methyl-(benzoxazolyl), 2-methyl-(1,3-thiazolyl), 2-methyl-(benzothiazolyl), 2-methyl-imidazolyl, 1,2-dimethyl-imidazolyl, 1-butyl-2-methyl-imidazolyl, 1-benzyl-2-methyl-imidazolyl, 2-methyl-1-phenyl-imidazolyl or 2-methyl-benzimidazolyl.
- 35 The $A-CR^{1B}R^{2B-}$ anion formed by deprotonation can be isolated and reacted with the fulvene (VI), but is preferably reacted with the fulvene (VI) without further isolation. As solvents for the further reaction, it is possible to use all aprotic solvents, in

particular aliphatic and aromatic hydrocarbons such as n-pentane, n-hexane, isohexane, n-heptane, isoheptane, decalin, benzene, toluene, ethylbenzene or xylene or ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, dimethoxyethane or diethylene glycol dimethyl ether and mixtures thereof. The subsequent reaction can be carried out at from -100 to +160°C, preferably from -80 to 100°C and particularly preferably from 0 to 60°C. At temperatures above 40°C, preference is given to using aromatic or aliphatic solvents which contain no ethers or only small proportions of ethers. The molar ratio of the A in $(A-CR^{1B}R^{2B})r(M^S X^S)_s^+$ to fulven (VI) is usually from 0.1:1 to 10:1, preferably 0.7:1 to 1.3:1 and particularly preferable 1:1 to 1.1:1.

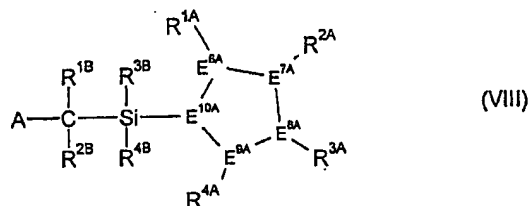
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The cyclopentadienyl system anions (V) obtained in this way can then be reacted further with the appropriate transition metal compound, e.g. chromium trichloride-tris-(tetrahydrofuran), to give the corresponding monocyclopentadienyl complex (A).

15 This process is particularly preferred to the other processes described. It can be used to synthesize a wide range of ligand structures. It is especially suitable for C₂-bridged ligand systems with A of the formula IIIa and IIIb. The yields with this process are very high and it is particularly suitable to upscale to larger amounts. Consequently the costs for this process are low.

20

Furthermore, we have found a process for preparing cyclopentadienyl systems of the formula (VIII):



25 where the variables have the following meanings:

$E^{6A}-E^{10A}$ are each carbon or not more than one E^{6A} to E^{10A} is phosphorus, where four adjacent $E^{6A}-E^{10A}$ form a conjugated diene system and the remaining $E^{6A}-E^{10A}$ additionally bears a hydrogen atom,

30

$R^{1A}-R^{4A}$ are each, independently of one another, hydrogen, C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, NR^{6A}_2 , $N(SiR^{6A}_3)_2$, OR^{6A} , $OSiR^{6A}_3$, SiR^{6A}_3 , where the organic radicals $R^{1A}-R^{4A}$

may also be substituted by halogens and two vicinal radicals R^{1A} - R^{4A} may also be joined to form a five- or six-membered ring, and/or two vicinal radicals R^{1A} - R^{4A} are joined to form a heterocycle which contains at least one atom from the group consisting of N, P, O and S,

5

R^{6A} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two geminal radicals R^{6A} may also be joined to form a five- or six-membered ring,

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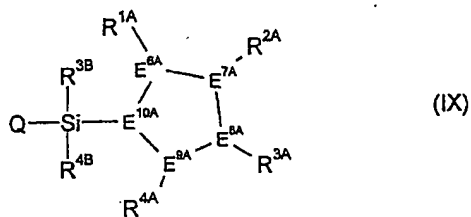
A is an unsubstituted, substituted or fused, heteroaromatic ring system,

R^{1B} - R^{4B} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{7B}_3 , where the organic radicals R^{1B} - R^{4B} may also be substituted by halogens and two geminal or vicinal radicals R^{1B} - R^{4B} may also be joined to form a five- or six-membered ring, and

15

20 R^{7B} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{7B} may also be joined to form a five- or six-membered ring,

25 which comprises reacting $(A-CR^{1B}R^{2B})_r(M^S X^S)_s^+$ with a cyclopentadienyl system of the formula (IX)



30 where the variables are as defined above and

Q is a leaving group, in particular chlorine, bromine, iodine, tosylate or triflate.

The preparation of the $A-CR^{1B}CR^{2B-}$ anions and their preferred embodiments have been described above and also apply in this process.

5 The cyclopentadienyl system (IX) can, for example, be prepared by reaction of the corresponding cyclopentadienyl system anion formed by removal of a single proton on one of the $E^{6A}-E^{10A}$ of a compound of the formula (IX) in which the group $SiR^{1B}R^{2B}Q$ is replaced by hydrogen with $SiR^{1B}R^{2B}Q_2$, where Q can be identical or different and are each a leaving group, in particular chlorine, bromine, iodine, tosylate or triflate. Such syntheses are described, for example, in EP-A-659757.

10 The $A-CR^{1B}R^{2B-}$ anion formed by deprotonation can be isolated and reacted with the cyclopentadienyl system (IX) but is preferably reacted with the cyclopentadienyl system (IX) without further isolation. As solvents, it is possible to use all aprotic solvents, in particular aliphatic and aromatic hydrocarbons such as n-pentane, n-hexane, isohexane, n-heptane, isohexane, decalin, benzene, toluene, ethylbenzene, 15 or xylene or ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, dimethoxyethane or diethylene glycol dimethyl ether and mixtures thereof. The reaction can be carried out at from -100 to +160°C, preferably from -80 to 100°C and particularly preferably from 0 to 60°C. At temperatures above 40°C, preference is 20 given to using aromatic or aliphatic solvents which contain no ethers or only small proportions of ethers.

The cyclopentadienyl system (VIII) obtained in this way can then be deprotonated by customary methods and be reacted further with the appropriate transition metal compound, e.g. chromium trichloride-tris(tetrahydrofuran), to give the corresponding 25 monocyclopentadienyl complex (A). Furthermore, the cyclopentadienyl system (VIII) can also, for example, be reacted directly with chromium amides to give the monocyclopentadienyl complex (A), using a method analogous to that in EP-A-742 046.

30 The monocyclopentadienyl complexes of the present invention can be used either alone or together with further components as catalyst system for olefin polymerization. We have also found catalyst systems for olefin polymerization comprising

35 A) at least one monocyclopentadienyl complex according to the present invention,

B) optionally, an organic or inorganic support,

- C) optionally, one or more activating compounds,
- D) optionally, one or more catalysts suitable for olefin polymerization and
- 5 E) optionally, one or more metal compounds containing a metal of group 1, 2 or 13 of the Periodic Table.

Thus, more than one of the monocyclopentadienyl complexes of the present invention can simultaneously be brought into contact with the olefin or olefins to be poly-
10 merized. This has the advantage that a wider range of polymers can be produced in this way. For example, bimodal products can be prepared in this way.

For the monocyclopentadienyl complexes of the present invention to be able to be used in polymerization processes in the gas phase or in suspension, it is often advantageous to use the metallocenes in the form of a solid, i.e. for them to be applied to a
15 solid support B). Furthermore, the supported monocyclopentadienyl complexes have a high productivity. The monocyclopentadienyl complexes of the present invention can therefore also, if desired, be immobilized on an organic or inorganic support B) and used in supported form in the polymerization. This enables, for example, deposits in
20 the reactor to be avoided and the polymer morphology to be controlled. As support materials, preference is given to using silica gel, magnesium chloride, aluminum oxide, mesoporous materials, aluminosilicates, hydrotalcites and organic polymers such as polyethylene, polypropylene, polystyrene, polytetrafluoroethylene or polar functionalized polymers, e.g. copolymers of ethene and acrylic esters, acrolein or
25 vinyl acetate.

Particular preference is given to a catalyst system comprising a monocyclopentadienyl complex according to the present invention and at least one activating compound C) and also a support component B).

30

To obtain such a supported catalyst system, the unsupported catalyst system can be reacted with a support component B). The order in which the support component B), the monocyclopentadienyl complex A) of the present invention and the activating compound C) are combined is in principle immaterial. The monocyclopentadienyl
35 complex A) of the present invention and the activating compound C) can be fixed to the support independently of one another or simultaneously. After the individual process steps, the solid can be washed with suitable inert solvents such as aliphatic or aromatic hydrocarbons.

In a preferred method of preparing the supported catalyst system, at least one of the monocyclopentadienyl complexes of the present invention is brought into contact with at least one activating compound C) in a suitable solvent, preferably giving a soluble reaction product, an adduct or a mixture. The preparation obtained in this way is then
 5 mixed with the dehydrated or passivated support material, the solvent is removed and the resulting supported monocyclopentadienyl complex catalyst system is dried to ensure that all or most of the solvent has been removed from the pores of the support material. The supported catalyst is obtained as a free-flowing powder. Examples of the industrial implementation of the above process are described in WO 96/00243,
 10 WO 98/40419 or WO 00/05277. A further preferred embodiment comprises firstly applying the activating compound C) to the support component B) and subsequently bringing this supported compound into contact with the monocyclopentadienyl complex A) of the present invention.

15 As support component B), preference is given to using finely divided supports which can be any organic or inorganic solids. In particular, the support component B) can be a porous support such as talc, a sheet silicate such as montmorillonite, mica, and inorganic oxide or a finely divided polymer powder (e.g. a polyolefin or a polymer having polar functional groups).

20 The support materials used preferably have a specific surface area in the range from 10 to 1 000 m²/g, a pore volume in the range from 0.1 to 5 ml/g and a mean particle size of from 1 to 500 µm. Preference is given to supports having a specific surface area in the range from 50 to 700 m²/g, a pore volume in the range from 0.4 to 3.5 ml/g
 25 and a mean particle size in the range from 5 to 350 µm. Particular preference is given to supports having a specific surface area in the range from 200 to 550 m²/g, a pore volume in the range from 0.5 to 3.0 ml/g and a mean particle size of from 10 to 150 µm.

30 The inorganic support can be subjected to a thermal treatment, e.g. to remove adsorbed water. Such a drying treatment is generally carried out at from 80 to 300°C, preferably from 100 to 200°C. Drying at from 100 to 200°C is preferably carried out under reduced pressure and/or under a blanket of inert gas (e.g. nitrogen), or the inorganic support can be calcined at from 200 to 1 000°C to produce the desired
 35 structure of the solid and/or the desired OH concentration on the surface. The support can also be treated chemically using customary desiccants such as metal alkyls, preferably aluminum alkyls, chlorosilanes or SiCl₄, or else methylaluminoxane. Appropriate treatment methods are described, for example, in WO 00/31090.

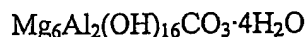
The inorganic support material can also be chemically modified. For example, the treatment of silica gel with NH_4SiF_6 or other fluorinating agents leads to fluorination of the silica gel surface, or treatment of silica gels with silanes containing nitrogen-,
 5 fluorine- or sulfur-containing groups leads to correspondingly modified silica gel surfaces.

Organic support materials such as finely divided polyolefin powders (e.g. polyethylene, polypropylene or polystyrene) can also be used and are preferably
 10 likewise freed of adhering moisture, solvent residues or other impurities by appropriate purification and drying operations before use. It is also possible to use functionalized polymer supports, e.g. ones based on polystyrene, polyethylene or polypropylene, via whose functional groups, for example ammonium or hydroxy groups, at least one of the catalyst components can be fixed.

15 Inorganic oxides suitable as support component B) may be found among the oxides of elements of groups 2, 3, 4, 5, 13, 14, 15 and 16 of the Periodic Table of the Elements. Examples of oxides preferred as supports include silicon dioxide, aluminum oxide and mixed oxides of the elements calcium, aluminum, silicon, magnesium or titanium and
 20 also corresponding oxide mixtures. Other inorganic oxides which can be used alone or in combination with the abovementioned preferred oxidic supports are, for example, MgO , CaO , AlPO_4 , ZrO_2 , TiO_2 , B_2O_3 or mixtures thereof.

As solid support materials B) for catalysts for olefin polymerization, preference is
 25 given to using silica gels since particles whose size and structure make them suitable as supports for olefin polymerization can be produced from this material. Spray-dried silica gels comprising spherical agglomerates of smaller granular particles, i.e. primary particles, have been found to be particularly useful. These silica gels can be dried and/or calcined before use.

30 Further preferred supports B) are hydrotalcites and calcined hydrotalcites. In mineralogy, hydrotalcite is a natural mineral having the ideal formula

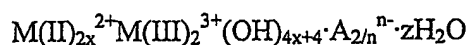


35 whose structure is derived from that of brucite $\text{Mg}(\text{OH})_2$. Brucite crystallizes in a sheet structure with the metal ions in octahedral holes between two layers of close-packed hydroxyl ions, with only every second layer of the octahedral holes being

occupied. In hydrotalcite, some magnesium ions are replaced by aluminum ions, as a result of which the packet of layers gains a positive charge. This is compensated by the anions which are located together with water of crystallization in the layers in between.

5

Such sheet structures are found not only in magnesium-aluminum hydroxides, but also generally in mixed metal hydroxides of the formula



10

which have a sheet structure and in which M(II) is a divalent metal such as Mg, Zn, Cu, Ni, Co, Mn, Ca and/or Fe and M(III) is a trivalent metal such as Al, Fe, Co, Mn, La, Ce and/or Cr, x is from 0.5 to 10 in steps of 0.5, A is an interstitial anion and n is the charge on the interstitial anion which can be from 1 to 8, usually from 1 to 4, and z is an integer from 1 to 6, in particular from 2 to 4. Possible interstitial anions are organic anions such as alkoxide anions, alkyl ether sulfates, aryl ether sulfates or glycol ether sulfates, inorganic anions such as, in particular, carbonate, hydrogencarbonate, nitrate, chloride, sulfate or $B(OH)_4^-$ or polyoxo metal anions such as $Mo_7O_{24}^{6-}$ or $V_{10}O_{28}^{6-}$. However, a mixture of a plurality of such anions can also be present.

20

Accordingly, all such mixed metal hydroxides having a sheet structure should be regarded as hydrotalcites for the purposes of the present invention.

Calcined hydrotalcites can be prepared from hydrotalcites by calcination, i.e. heating, by means of which the desired hydroxyl group content can be set. In addition, the crystal structure also changes. The preparation of the calcined hydrotalcites used according to the present invention is usually carried out at temperatures above 180°C. Preference is given to calcination for from 3 to 24 hours at from 250°C to 1 000°C, in particular from 400°C to 700°C. It is possible for air or inert gas to be passed over the solid during calcination or for a vacuum to be applied.

30

On heating, the natural or synthetic hydrotalcites firstly give off water, i.e. drying occurs. On further heating, the actual calcination, the metal hydroxides are converted into the metal oxides by elimination of hydroxyl groups and interstitial anions; OH groups or interstitial anions such as carbonate can also still be present in the calcined hydrotalcites. A measure of this is the loss on ignition. This is the weight loss experienced by a sample which is heated in two steps firstly for 30 minutes at 200°C in a drying oven and then for 1 hour at 950°C in a muffle furnace.

35

The calcined hydrotalcites used as component B) are thus mixed oxides of the divalent and trivalent metals M(II) and M(III), with the molar ratio of M(II) to M(III) generally being in the range from 0.5 to 10, preferably from 0.75 to 8 and in particular from 1 to 4. Furthermore, normal amounts of impurities, for example Si, Fe, Na, Ca or Ti and also chlorides and sulfates, can also be present.

Preferred calcined hydrotalcites B) are mixed oxides in which M(II) is magnesium and M(III) is aluminum. Such aluminum-magnesium mixed oxides are obtainable from Condea Chemie GmbH (now Sasol Chemie), Hamburg, under the trade name Puralox Mg.

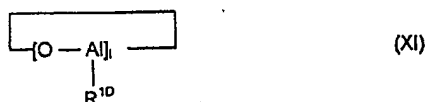
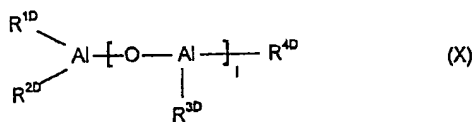
Preference is also given to calcined hydrotalcites in which the structural transformation is complete or virtually complete. Calcination, i.e. transformation of the structure, can be confirmed, for example, by means of X-ray diffraction patterns.

The hydrotalcites, calcined hydrotalcites or silica gels employed are generally used as finely divided powders having a mean particle diameter d_{50} of from 5 to 200 μm , preferably from 10 to 150 μm , particularly preferably from 15 to 100 μm and in particular from 20 to 70 μm , and usually have pore volumes of from 0.1 to 10 cm^3/g , preferably from 0.2 to 5 cm^3/g , and specific surface areas of from 30 to 1 000 m^2/g , preferably from 50 to 800 m^2/g and in particular from 100 to 600 m^2/g . The monocyclopentadienyl complexes of the present invention are preferably applied in such an amount that the concentration of monocyclopentadienyl complexes in the finished catalyst system is from 5 to 200 μmol , preferably from 20 to 100 μmol and particularly preferably from 25 to 70 μmol per g of support B).

Some of the monocyclopentadienyl complexes of the present invention have little polymerization activity on their own and are then brought into contact with an activator, viz. the component C), to be able to display good polymerization activity. For this reason, the catalyst system optionally further comprises, as component C), one or more activating compounds, preferably at least one cation-forming compound C).

Suitable compounds C) which are able to react with the monocyclopentadienyl complex A) to convert it into a catalytically active, or more active, compound are, for example, compounds such as an aluminoxane, a strong uncharged Lewis acid, an ionic compound having a Lewis-acid cation or an ionic compound containing a Brönsted acid as cation.

As aluminoxanes, it is possible to use, for example, the compounds described in WO 00/31090. Particularly useful aluminoxanes are open-chain or cyclic aluminoxane compounds of the formula (X) or (XI)



where R^{1D} - R^{4D} are each, independently of one another, a C_1 - C_6 -alkyl group, preferably a methyl, ethyl, butyl or isobutyl group, and l is an integer from 1 to 30, preferably from 5 to 25.

A particularly useful aluminoxane compound is methylaluminoxane.

These oligomeric aluminoxane compounds are usually prepared by controlled reaction of a solution of trialkylaluminum with water. In general, the oligomeric aluminoxane compounds obtained in this way are in the form of mixtures of both linear and cyclic chain molecules of various lengths, so that l is to be regarded as a mean. The aluminoxane compounds can also be present in admixture with other metal alkyls, usually aluminum alkyls. Aluminoxane preparations suitable as component C) are commercially available.

Furthermore, modified aluminoxanes in which some of the hydrocarbon radicals have been replaced by hydrogen atoms or alkoxy, aryloxy, siloxy or amide radicals can also be used as component C) in place of the aluminoxane compounds of the formula (X) or (XI).

It has been found to be advantageous to use the monocyclopentadienyl complexes A) and the aluminoxane compounds in such amounts that the atomic ratio of aluminum from the aluminoxane compounds including any aluminum alkyl still present to the transition metal from the monocyclopentadienyl complex A) is in the range from 1:1 to 1 000:1, preferably from 10:1 to 500:1 and in particular in the range from 20:1 to 400:1.

A further class of suitable activating components C) are hydroxyaluminoxanes. These

can be prepared, for example, by addition of from 0.5 to 1.2 equivalents of water, preferably from 0.8 to 1.2 equivalents of water, per equivalent of aluminum to an alkyl-aluminum compound, in particular triisobutylaluminum, at low temperatures, usually below 0°C. Such compounds and their use in olefin polymerization are described, for example, in WO 00/24787. The atomic ratio of aluminum from the hydroxyaluminoxane compound to the transition metal from the monocyclopentadienyl complex A) is usually in the range from 1:1 to 100:1, preferably from 1:1 to 50:1 and in particular in the range from 20:1 to 40:1. Preference is given to using a monocyclopentadienyl metal dialkyl compound A).

10

As strong, uncharged Lewis acids, preference is given to compounds of the formula (XII)



15

where

M^{2D} is an element of group 13 of the Periodic Table of the Elements, in particular B, Al or Ga, preferably B,

20

X^{1D} , X^{2D} and X^{3D} are each hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical or fluorine, chlorine, bromine or iodine, in particular haloaryls, preferably pentafluorophenyl.

25

Further examples of strong, uncharged Lewis acids are given in WO 00/31090.

Compounds of this type which are particularly useful as component C) are boranes and boroxins such as trialkylborane, triarylborane or trimethylboroxin. Particular preference is given to using boranes which bear at least two perfluorinated aryl radicals. Particular preference is given to compounds of the formula (XII) in which X^{1D} , X^{2D} and X^{3D} are identical, preferably tris(pentafluorophenyl)borane.

30

Suitable compounds C) are preferably prepared by reaction of aluminum or boron compounds of the formula (XII) with water, alcohols, phenol derivatives, thiophenol derivatives or aniline derivatives, with halogenated and especially perfluorinated alcohols and phenols being of particular importance. Examples of particularly useful compounds are pentafluorophenol, 1,1-bis(pentafluorophenyl)methanol and 4-hydroxy-

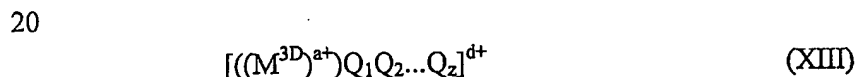
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2,2',3,3',4,4',5,5',6,6'-noafluorobiphenyl. Examples of combinations of compounds of the formula (XII) with Brönsted acids are, in particular, trimethylaluminum/pentafluorophenol, trimethylaluminum/1-bis(pentafluorophenyl)methanol, trimethylaluminum/4-hydroxy-2,2',3,3',4,4',5,5',6,6'-nonafluorobiphenyl, triethylaluminum/pentafluorophenol and triisobutylaluminum/pentafluorophenol and triethylaluminum/4,4'-dihydroxy-2,2',3,3',5,5',6,6'-octafluorobiphenyl hydrate.

In further suitable aluminum and boron compounds of the formula (XII), R^{1D} is an OH group. Examples of compounds of this type are boronic acids and borinic acids, in particular borinic acids having perfluorinated aryl radicals, for example (C₆H₅)₂BOH.

Strong uncharged Lewis acids suitable as activating compounds C) also include the reaction products of a boronic acid with two equivalents of an aluminum trialkyl or the reaction products of an aluminum trialkyl with two equivalents of an acidic fluorinated, in particular perfluorinated, hydrocarbon compound such as pentafluorophenol or bis(pentafluorophenyl)borinic acid.

The suitable ionic compounds having Lewis acid cations include salt-like compounds of the cation of the formula (XIII)



where

25 M^{3D} is an element of groups 1 to 16 of the Periodic Table of the Elements,

Q_1 to Q_z are singly negatively charged groups such as C₁-C₂₈-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl, haloalkyl, haloaryl each having from 6 to 20 carbon atoms in the aryl radical and from 1 to 28 carbon atoms in the alkyl radical, C₃-C₁₀-cycloalkyl which may bear C₁-C₁₀-alkyl groups as substituents, halogen, C₁-C₂₈-alkoxy, C₆-C₁₅-aryloxy, silyl or mercaptyl groups,

35 a is an integer from 1 to 6 and

z is an integer from 0 to 5,

d corresponds to the difference a-z, but d is greater than or equal to 1.

Particularly useful cations are carbonium cations, oxonium cations and sulfonium cations and also cationic transition metal complexes. Particular mention may be made of the triphenylmethyl cation, the silver cation and the 1,1'-dimethylferrocenyl cation.

- 5 They preferably have noncoordinating counterions, in particular boron compounds as are also mentioned in WO 91/09882, preferably tetrakis(pentafluorophenyl)borate.

- Salts having noncoordinating anions can also be prepared by combining a boron or aluminum compound, e.g. an aluminum alkyl, with a second compound which can
 10 react to link two or more boron or aluminum atoms, e.g. water, and a third compound which forms an ionizing ionic compound with the boron or aluminum compound, e.g. triphenylchloromethane, or optionally a base, preferably an organic nitrogen-containing base, for example an amine, an aniline derivative or a nitrogen heterocycle. In addition, a fourth compound which likewise reacts with the boron or aluminum
 15 compound, e.g. pentafluorophenol, can be added.

- Ionic compounds containing Brönsted acids as cations preferably likewise have noncoordinating counterions. As Brönsted acid, particular preference is given to protonated amine or aniline derivatives. Preferred cations are N,N-dimethylanilinium,
 20 N,N-dimethylcyclohexylammonium and N,N-dimethylbenzylammonium and also derivatives of the latter two.

- Compounds containing anionic boron heterocycles as are described in WO 97/36937 are also suitable as component C), in particular dimethylanilinium boratabenzene or
 25 trityl boratabenzene.

- Preferred ionic compounds C) contain borates which bear at least two perfluorinated aryl radicals. Particular preference is given to N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and in particular N,N-dimethylcyclohexylammonium tetrakis-
 30 (pentafluorophenyl)borate, N,N-dimethylbenzylammonium tetrakis(pentafluorophenyl)borate or trityl tetrakis(pentafluorophenyl)borate.

- It is also possible for two or more borate anions to be joined to one another, as in the dianion $[(C_6F_5)_2B-C_6F_4-B(C_6F_5)_2]^{2-}$, or the borate anion can be bound via a bridge to a
 35 suitable functional group on the support surface.

Further suitable activating compounds C) are listed in WO 00/31090.

The amount of strong, uncharged Lewis acids, ionic compounds having Lewis-acid cations or ionic compounds containing Brönsted acids as cations is preferably from 0.1 to 20 equivalents, more preferably from 1 to 10 equivalents, based on the monocyclopentadienyl complex A).

5

Suitable activating compounds C) also include boron-aluminum compounds such as di[bis(pentafluorophenyl)boroxy]methylalane. Examples of such boron-aluminum compounds are those disclosed in WO 99/06414.

- 10 It is also possible to use mixtures of all the abovementioned activating compounds C). Preferred mixtures comprise aluminoxanes, in particular methylaluminoxane, and an ionic compound, in particular one containing the tetrakis(pentafluorophenyl)borate anion, and/or a strong uncharged Lewis acid, in particular tris(pentafluorophenyl)-borane.

15

Both the monocyclopentadienyl complexes A) and the activating compounds C) are preferably used in a solvent, preferably an aromatic hydrocarbon having from 6 to 20 carbon atoms, in particular xylenes, toluene, pentane, hexane, heptane or a mixture thereof.

20

A further possibility is to use an activating compound C) which can simultaneously be employed as support B). Such systems are obtained, for example, from an inorganic oxide by treatment with zirconium alkoxide and subsequent chlorination, for example by means of carbon tetrachloride. The preparation of such systems is described, for example, in WO 01/41920.

25

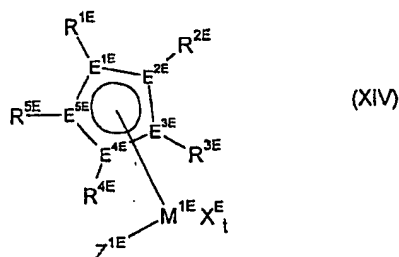
A likewise broad product spectrum can be achieved by use of the monocyclopentadienyl complexes A) of the present invention in combination with at least one further catalyst D) which is suitable for the polymerization of olefins. It is therefore possible to use one or more catalysts suitable for olefin polymerization as optional component D) in the catalyst system. Possible catalysts D) are, in particular, classical Ziegler-Natta catalysts based on titanium and classical Phillips catalysts based on chromium oxides.

30

- 35 Possible components D) are in principle all compounds of transition metals of groups III to XII of the Periodic Table or the lanthanides which contain organic groups and preferably form active catalysts for olefin polymerization after reaction with the components C) in the presence of A) and optionally B) and/or E). These are usually

compounds in which at least one monodentate or polydentate ligand is bound to the central atom via a sigma or pi bond. Possible ligands include both ligands containing cyclopentadienyl groups and ligands which are free of cyclopentadienyl groups. A large number of such compounds D) suitable for olefin polymerization are described in Chem. Rev. 2000, vol, 100, No. 4. Furthermore, multinuclear cyclopentadienyl complexes are also suitable for olefin polymerization.

Particularly well-suited components D) include compounds having at least one cyclopentadienyl ligand, which are generally referred to a metallocene complexes. Particularly useful metallocene complexes are those of the formula (XIV)



where the substituents and indices have the following meanings:

- 15 M^{1E} is titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten, or an element of group 3 of the Periodic Table and the lanthanides,
- 20 X^E is fluorine, chlorine, bromine, iodine, hydrogen, C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_6 - C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, $-OR^{6E}$ or $-NR^{6E}R^{7E}$, or two radicals X^E form a substituted or unsubstituted diene ligand, in particular a 1,3-diene ligand, and the radicals X^E are identical or
- 25 different and may be joined to one another,
- $E^{1E}-E^{5E}$ are each carbon or not more than one E^{1E} to E^{5E} is phosphorus or nitrogen, preferably carbon,
- 30 t is 1, 2 or 3 and is such that, depending on the valence of M^{1E} , the metallocene complex of the formula (XIV) is uncharged,

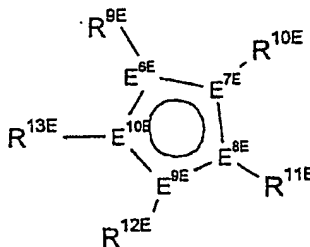
where

R^{6E} and R^{7E} are each C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl, each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical, and

5 R^{1E} to R^{5E} are each, independently of one another, hydrogen, C_1 - C_{22} -alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl which may in turn bear C_1 - C_{10} -alkyl groups as substituents, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl having from 1 to 16 carbon atoms in the alkyl part and 6-21 carbon atoms in the aryl part, NR^{8E}_2 , $N(SiR^{8E}_3)_2$, OR^{8E} , $OSiR^{8E}_3$, SiR^{8E}_3 , where the organic radicals R^{1E} - R^{5E} may also be substituted by halogens and/or two radicals R^{1E} - R^{5E} , in particular vicinal radicals, may also be joined to form a 5-, 6- or 7-membered ring, and/or two vicinal radicals R^{1E} - R^{5E} may be joined to form a five-, six- or seven-membered heterocycle which
15 contains at least one atom from the group consisting of N, P, O and S, where

R^{8E} can be identical or different and are each C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl, C_6 - C_{15} -aryl, C_1 - C_4 -alkoxy or C_6 - C_{10} -aryloxy and

20 Z^{1E} is as defined for X^E or is



where the radicals

25 R^{9E} to R^{13E} are each, independently of one another, hydrogen, C_1 - C_{22} -alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl which may in turn bear C_1 - C_{10} -alkyl groups as substituents, C_2 - C_{22} -alkenyl, C_6 - C_{22} -aryl, arylalkyl having from 1 to 16 carbon atoms in the alkyl part and 6-21 carbon atoms in the aryl part, NR^{14E}_2 , $N(SiR^{14E}_3)_2$, OR^{14E} , $OSiR^{14E}_3$, SiR^{14E}_3 , where the organic radicals R^{9E} - R^{13E} may also be substituted by halogens and/or two radicals R^{9E} - R^{13E} , in particular vicinal radicals, may also be joined to form a five-, six- or seven-membered ring, and/or two vicinal radicals R^{9E} - R^{13E} may be joined to form a five-, six- or seven-membered heterocycle which
30

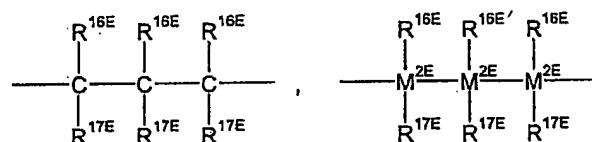
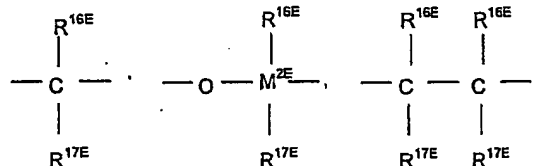
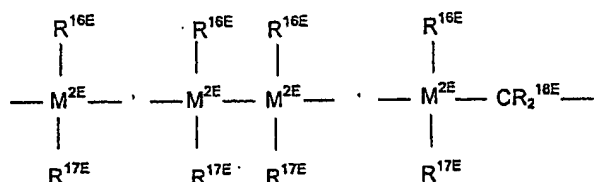
contains at least one atom from the group consisting of N, P, O and S,
where

5 R^{14E} are identical or different and are each C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl, C_6 - C_{15} -aryl, C_1 - C_4 -alkoxy or C_6 - C_{10} -aryloxy,

E^{6E} - E^{10E} are each carbon or not more than one E^{6E} to E^{10E} is phosphorus or nitrogen, preferably carbon,

10 or the radicals R^{4E} and Z^{1E} together form an $-R^{15E}_v-A^{1E}$ - group in which

R^{15E} is



15

$=BR^{16E}$, $=BNR^{16E}R^{17E}$, $=AIR^{16E}$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $=SO$, $=SO_2$, $=NR^{16E}$, $=CO$,
 $=PR^{16E}$ or $=P(O)R^{16E}$,

where

20

R^{16E} , R^{17E} and R^{18E} are identical or different and are each a hydrogen atom, a halogen atom, a trimethylsilyl group, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a C_6 - C_{10} -fluoroaryl group, a C_6 - C_{10} -aryl group, a C_1 - C_{10} -alkoxy group, a C_7 - C_{15} -alkylaryloxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_8 - C_{40} -arylalkenyl group or a C_7 - C_{40} -alkylaryl group or two adjacent radicals together with the atoms connecting them form a saturated or unsaturated ring having from 4 to 15 carbon atoms,

25

and

M^{2E} is silicon, germanium or tin, preferably silicon,

5 A^{1E} is

— O —, — S —, >NR^{19E} , >PR^{18E} , =O, =S, =NR^{19E}, — O — R^{19E},
 $-\text{NR}^{19E}_2$, $-\text{PR}^{19E}_2$ or an unsubstituted, substituted or fused, heterocyclic
 ring system, where

10 R^{19E} are each, independently of one another, C₁-C₁₀-alkyl, C₆-C₁₅-aryl,
 C₃-C₁₀-cycloalkyl, C₇-C₁₈-alkylaryl or Si(R^{20E})₃,

R^{20E} is hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl which may in turn bear C₁-C₄-alkyl
 groups as substituents or C₃-C₁₀-cycloalkyl,

15

v is 1 or when A^{1E} is an unsubstituted, substituted or fused, heterocyclic
 ring system may also be 0,
 or the radicals R^{4E} and R^{12E} together form an -R^{15E}- group.

20 A^{1E} together with the bridge R^{15E} can, for example, form an amine, ether, thioether or
 phosphine. However, A^{1E} may also be an unsubstituted, substituted or fused, hetero-
 cyclic aromatic ring system which can contain heteroatoms from the group consisting
 of oxygen, sulfur, nitrogen and phosphorus in addition to carbon atoms in the ring.
 Examples of five-membered heteroaryl groups which can contain from 1 to 4 nitrogen

25 atoms and/or a sulfur or oxygen atom as ring atoms in addition to carbon atoms are
 2-furyl, 2-thienyl, 2-pyrrolyl, 3-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 5-isothiazolyl,
 1-pyrazolyl, 3-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl,
 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 1,2,4-oxadiazol-3-
 yl, 1,2,4-oxadiazol-5-yl, 1,3,4-oxadiazol-2-yl or 1,2,4-triazol-3-yl. Examples of

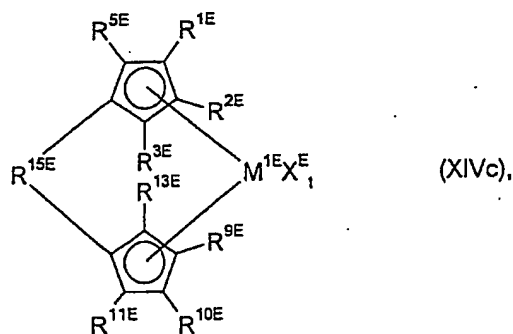
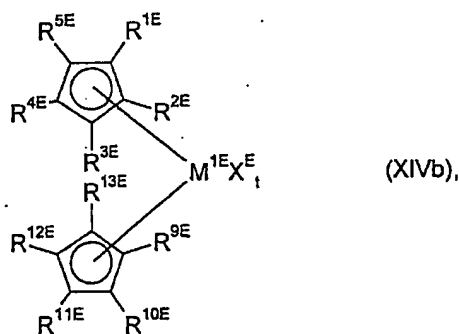
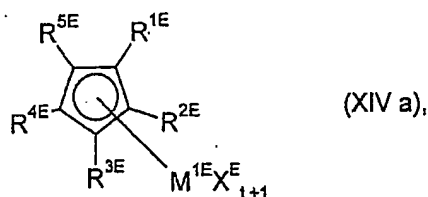
30 6-membered heteroaryl groups, which can contain from 1 to 4 nitrogen atoms and/or a
 phosphorus atom, are 2-pyridinyl, 2-phosphabenzolyl, 3-pyridazinyl, 2-pyrimidinyl,
 4-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-1-yl and 1,2,4-triazin-3-yl, 1,2,4-triazin-5-yl
 and 1,2,4-triazin-6-yl. The 5-membered and 6-membered heteroaryl groups can also
 be substituted by C₁-C₁₀-alkyl, C₆-C₁₀-aryl, alkylaryl having from 1 to 10 carbon
 35 atoms in the alkyl part and 6-10 carbon atoms in the aryl part, trialkylsilyl or halogens
 such as fluorine, chlorine or bromine or be fused with one or more aromatics or he-
 teroaromatics. Examples of benzo-fused 5-membered heteroaryl groups are 2-indolyl,
 7-indolyl, 2-coumaronyl, 7-coumaronyl, 2-thianaphthenyl, 7-thianaphthenyl, 3-in-

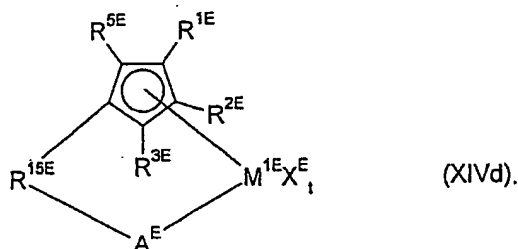
dazolyl, 7-indazolyl, 2-benzimidazolyl and 7-benzimidazolyl. Examples of benzo-fused 6-membered heteroaryl groups are 2-quinolyl, 8-quinolyl, 3-cinnolyl, 8-cinnolyl, 1-phthalazyl, 2-quinazolyl, 4-quinazolyl, 8-quinazolyl, 5-quinoxalyl, 4-acridyl, 1-phenanthridyl and 1-phenazyl. Nomenclature and numbering of the heterocycles has
 5 been taken from L. Fieser and M. Fieser, *Lehrbuch der organischen Chemie*, 3rd revised edition, Verlag Chemie, Weinheim 1957.

It is preferred that the radicals X^E in the formula (XIV) are identical, preferably
 10 fluorine, chlorine, bromine, C_1 - C_7 -alkyl or aralkyl, in particular chlorine, methyl or benzyl.

The synthesis of such complexes can be carried out by methods known per se, preferably by reaction of the appropriately substituted, cyclic hydrocarbon anions with
 15 halides of titanium, zirconium, hafnium or chromium.

Among the metallocene complexes of the formula (XIV), preference is given to





Among the compounds of the formula (XIVa), particular preference is given to those in which

- 5 M^{1E} is titanium, vanadium or chromium,
 X^E is chlorine, C_1 - C_4 -alkyl, phenyl, alkoxy or aryloxy,
 t is 1 or 2 and
 R^{1E} to R^{5E} are each hydrogen or C_1 - C_6 -alkyl or two adjacent radicals R^{1E} to R^{5E} form a substituted or unsubstituted benzo group.

10

Among the compounds of the formula (XIVb), preference is given to those in which

- M^{1E} is titanium, zirconium, vanadium, hafnium or chromium,
 X^E is fluorine, chlorine, C_1 - C_4 -alkyl or benzyl, or two radicals X^E form a substituted or unsubstituted butadiene ligand,
 15 t is 0 in the case of chromium, otherwise 1 or 2, preferably 2,
 R^{1E} to R^{5E} are each hydrogen, C_1 - C_8 -alkyl, C_6 - C_8 -aryl, NR^{8E}_2 , $OSiR^{8E}_3$ or $Si(R^{8E})_3$
 and
 R^{9E} to R^{13E} are each hydrogen, C_1 - C_8 -alkyl or C_6 - C_8 -aryl, NR^{14E}_2 , $OSiR^{14E}_3$ or $Si(R^{14E})_3$
 20 or two radicals R^{1E} to R^{5E} and/or R^{9E} to R^{13E} together with the C_5 ring form an indenyl or substituted indenyl system.

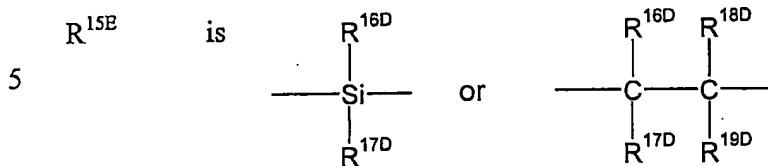
The compounds of the formula (XIVb) in which the cyclopentadienyl radicals are identical are particularly useful.

25

Examples of particularly useful compounds D) of the formula (XIVb) include:

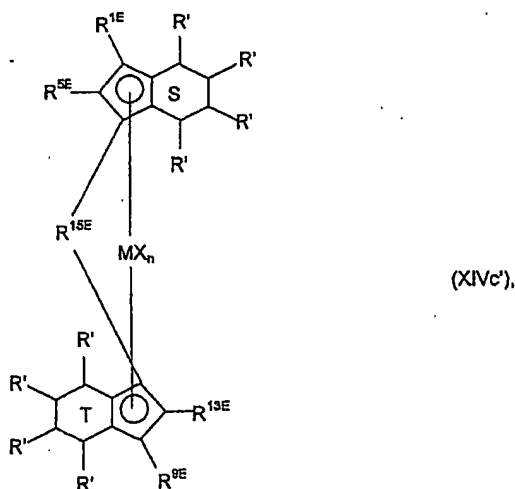
- bis(cyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, bis(ethylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis-(1-n-butyl-3-methylcyclopentadienyl)zirconium dichloride, bis(indenyl)zirconium dichloride, bis(tetrahydroindenyl)zirconium dichloride and bis(trimethylsilylcyclopentadienyl)zirconium dichloride and also the corresponding dimethylzirconium compounds.
- 30

Particularly useful compounds of the formula (XIVc) are those in which



10 M^{1E} is titanium, zirconium or hafnium, in particular zirconium, and
 X^E are identical or different and are each chlorine, C_1 - C_4 -alkyl, benzyl, phenyl or C_7 - C_{15} -alkylaryloxy.

Particularly useful compounds of the formula (XIVc) are those of the formula (XIVc')



15

where

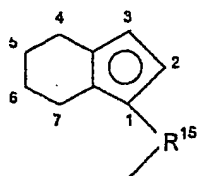
the radicals R' are identical or different and are each hydrogen, C_1 - C_{10} -alkyl or C_3 - C_{10} -cycloalkyl, preferably methyl, ethyl, isopropyl or cyclohexyl, C_6 - C_{20} -aryl, preferably phenyl, naphthyl or mesityl, C_7 - C_{40} -arylalkyl, C_7 - C_{40} -alkylaryl, preferably
 20 4-tert-butylphenyl or 3,5-di-tert-butylphenyl, or C_8 - C_{40} -arylalkenyl,

R^{5E} and R^{13E} are identical or different and are each hydrogen, C_1 - C_6 -alkyl, preferably methyl, ethyl, isopropyl, n-propyl, n-butyl, n-hexyl or tert-butyl, and the rings S and T may be identical or different and saturated, unsaturated or partially saturated.

25

The indenyl or tetrahydroindenyl ligands of the metallocenes of the formula (XIVc') are preferably substituted in the 2 position, the 2,4 positions, the 4,7 positions, the 2,4,7 positions, the 2,6 positions, the 2,4,6 positions, the 2,5,6 positions, the 2,4,5,6

positions or the 2,4,5,6,7 positions, in particular in the 2,4 positions, with the following numbering applying to the site of substitution:



Furthermore, preference is given to using bridged bis-indenyl complexes in the rac or pseudo-rac form as component D). The term "pseudo-rac form" refers to complexes in which the two indenyl ligands are in the rac arrangement relative to one another when all other substituents of the complex are disregarded.

- Further examples of particularly useful catalysts D) (XIVc) and (XIVc') include:
- 10 dimethylsilanediylbis(cyclopentadienyl)zirconium dichloride, dimethylsilanediylbis(indenyl)zirconium dichloride, dimethylsilanediylbis(tetrahydroindenyl)zirconium dichloride, ethylenebis(cyclopentadienyl)zirconium dichloride, ethylenebis(indenyl)zirconium dichloride, ethylenebis(tetrahydroindenyl)zirconium dichloride, tetramethylethylene-9-fluoroenylcyclopentadienyl)zirconium dichloride, dimethylsilanediyl-
 - 15 bis(3-tert-butyl-5-methylcyclopentadienyl)zirconium dichloride, dimethylsilanediylbis(3-tert-butyl-5-ethylcyclopentadienyl)zirconium dichloride, dimethylsilanediylbis(2-methylindenyl)zirconium dichloride, dimethylsilanediylbis(2-isopropylindenyl)zirconium dichloride, dimethylsilanediylbis(2-tert-butylindenyl)zirconium dichloride, diethylsilanediylbis(2-methylindenyl)zirconium dibromide, dimethylsilanediylbis-
 - 20 (3-methyl-5-methylcyclopentadienyl)zirconium dichloride, dimethylsilanediylbis(3-ethyl-5-isopropylcyclopentadienyl)zirconium dichloride, dimethylsilanediylbis(2-ethylindenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride, dimethylsilanediylbis(2-ethyl-4,5-benzindenyl)zirconium dichloride, methylphenylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride, methylphenylsilanediylbis(2-ethyl-4,5-benzindenyl)zirconium dichloride, diphenylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride, diphenylsilanediylbis(2-ethyl-4,5-benzindenyl)zirconium dichloride, diphenylsilanediylbis(2-methylindenyl)hafnium dichloride, dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride, dimethylsilanediylbis(2-ethyl-4-phenylindenyl)zirconium dichloride,
 - 25 dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)zirconium dichloride, dimethylsilanediylbis(2-ethyl-4-(1-naphthyl)indenyl)zirconium dichloride, dimethylsilanediylbis(2-propyl-4-(1-naphthyl)indenyl)zirconium dichloride, dimethylsilanediylbis(2-isobutyl-4-(1-naphthyl)indenyl)zirconium dichloride, dimethylsilanediylbis(2-propyl-4-(9-phenanthryl)indenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4-iso-
 - 30

propylindenyl)zirconium dichloride, dimethylsilanediylbis(2,7-dimethyl-4-isopropylindenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4-[p-trifluoromethylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4-[3',5'-dimethylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, diethylsilanediylbis(2-methyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-ethyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-propyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-isopropyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-n-butyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediylbis(2-hexyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediyl (2-isopropyl-4-phenylindenyl)(2-methyl-4-phenylindenyl)zirconium dichloride, dimethylsilanediyl(2-isopropyl-4-(1-naphthyl)indenyl)(2-methyl-4-(1-naphthyl)indenyl)zirconium dichloride, dimethylsilanediyl(2-isopropyl-4-[4'-tert-butylphenyl]indenyl)(2-methyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediyl(2-isopropyl-4-[4'-tert-butylphenyl]indenyl)(2-ethyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediyl(2-isopropyl-4-[4'-tert-butylphenyl]indenyl)(2-methyl-4-[3',5'-bis-tert-butylphenyl]indenyl)zirconium dichloride, dimethylsilanediyl(2-isopropyl-4-[4'-tert-butylphenyl]indenyl)(2-methyl-4-[1'-naphthyl]indenyl)zirconium dichloride and ethylene(2-isopropyl-4-[4'-tert-butylphenyl]indenyl)(2-methyl-4-[4'-tert-butylphenyl]indenyl)zirconium dichloride, and also the corresponding dimethylzirconium, zirconium monochloride mono(alkylaryloxy) and zirconium di(alkylaryloxy) compounds. The complexes are preferably used in the rac form.

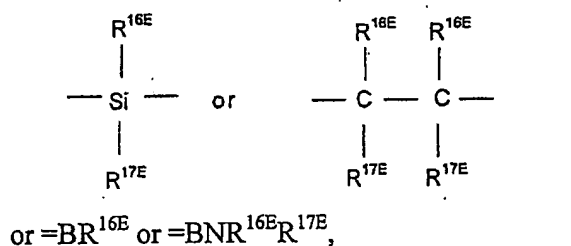
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Such complexes can be synthesized by methods known per se, preferably by reaction of the appropriately substituted, cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium, tantalum or chromium. Examples of appropriate preparative methods are described, inter alia, in Journal of Organometallic Chemistry, 369 (1989), 359-370.

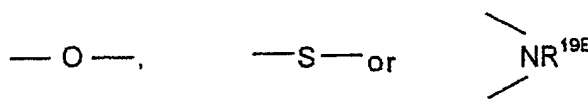
30

Particularly useful compounds of the formula (XIVd) are those in which

M^{1E} is titanium or zirconium, in particular titanium, and
 X^E is chlorine, C_1 - C_4 -alkyl or phenyl or two radicals X form a substituted or
 35 unsubstituted butadiene ligand,
 R^{15E} is



A^{1E} is



t is 1 or 2, preferably 2,

- 10 R^{1E} to R^{3E} and R^{5E} are each hydrogen, C₁-C₁₀-alkyl, preferably methyl, C₃-C₁₀-cycloalkyl, C₆-C₁₅-aryl, NR^{8E}₂ or Si(R⁸)₃, or two adjacent radicals form a cyclic group having from 4 to 12 carbon atoms, with particular preference being given to all R^{1E} to R^{3E} and R^{5E} being methyl.

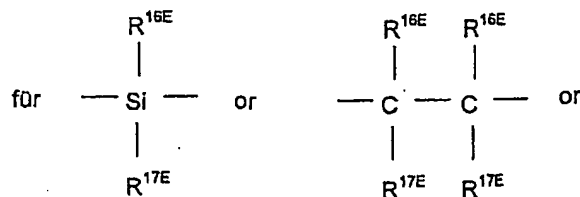
- 15 Particularly useful complexes D) of the formula (XIVd) are dimethylsilanediyl(tetramethylcyclopentadienyl)(benzylamino)titanium dichloride, dimethylsilanediyl(tetramethylcyclopentadienyl)(tert-butylamino)titanium dichloride, dimethylsilanediyl-(tetramethylcyclopentadienyl)(adamantyl)titanium dichloride and dimethylsilanediyl-(indenyl)(tert-butylamino)titanium dichloride.

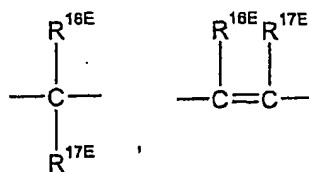
- 20 Another group of compounds of the formula (XIVd) which are particularly useful are those in which

M^{1E} is titanium, vanadium or chromium, preferably in the oxidation state III, and

- 25 X^E is chlorine, C₁-C₄-alkyl or phenyl or two radicals X^E form a substituted or unsubstituted butadiene ligand,

R^{15E} is





, or $=BR^{16E}$ or $=BNR^{16E}R^{17E}$,

A^{1E} is $-O-R^{19E}$, $-NR^{19E}_2$, $-PR^{19E}_2$ or an unsubstituted, substituted or fused, heterocyclic, in particular heteroaromatic, ring system,

5

v is 1 or when A^{1E} is an unsubstituted, substituted or fused, heterocyclic ring system may be 0 or 1,

R^{1E} to R^{3E} and R^{5E} are each hydrogen, C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl, C_6 - C_{15} -aryl or $Si(R^{8E})_3$, or two adjacent radicals form a cyclic group having from 4 to 12 carbon atoms.

In a preferred embodiment, A^{1E} is an unsubstituted, substituted or fused, heteroaromatic ring system and M^{1E} is chromium. Very particular preference is given to A^{1E} being an unsubstituted or substituted, e.g. alkyl-substituted quinolyl or pyridyl bound in position 8 or 2, e.g. 8-quinolyl, 8-(2-methylquinolyl), 8-(2,3,4-trimethylquinolyl), 8-(2,3,4,5,6,7-hexamethylquinolyl), v being 0 and M^{1E} being chromium. Preferred catalysts D) of this type are 1-(8-quinolyl)-2-methyl-4-methylcyclopentadienylchromium(III) dichloride, 1-(8-quinolyl)-3-isopropyl-5-methylcyclopentadienylchromium(III) dichloride, 1-(8-quinolyl)-3-tert-butyl-5-methylcyclopentadienylchromium(III) dichloride, 1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadienylchromium(III) dichloride, 1-(8-quinolyl)tetrahydroindenylchromium(III) dichloride, 1-(8-quinolyl)indenylchromium(III) dichloride, 1-(8-quinolyl)-2-methylindenylchromium(III) dichloride, 1-(8-quinolyl)-2-isopropylindenylchromium(III) dichloride, 1-(8-quinolyl)-2-ethylindenylchromium(III) dichloride, 1-(8-quinolyl)-2-tert-butylindenylchromium(III) dichloride, 1-(8-quinolyl)benzindenylchromium(III) dichloride, 1-(8-quinolyl)-2-methylbenzindenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))-2-methyl-4-methylcyclopentadienylchromium(III) dichloride, 1-(8-(2-methylquinolyl))-2,3,4,5-tetramethylcyclopentadienylchromium(III) dichloride, 1-(8-(2-methylquinolyl))tetrahydroindenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))indenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))-2-methylindenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))-2-isopropylindenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))-2-ethylindenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))-2-tert-butylindenylchromium(III) dichloride, 1-(8-(2-methylquinolyl))benzindenylchromium(III) dichloride or 1-(8-(2-methylquinolyl))-2-methylbenzindenylchromi-

um(III) dichloride.

Furthermore, owing to the ease of preparation, preference is given to compounds in which R^{15E} is $CH=CH$ or 1,2-phenylene and A^{1E} is NR^{19E}_2 , and compounds in which
 5 R^{15E} is CH_2 , $C(CH_3)_2$ or $Si(CH_3)_2$ and A^{1E} is unsubstituted or substituted 8-quinolyl or unsubstituted or substituted 2-pyridyl.

The preparation of such functional cyclopentadienyl ligands has been known for a long time. Various synthetic routes to these complexing ligands are described, for
 10 example, by M. Enders et al. in Chem. Ber. (1996), 129, 459-463, or P. Jutzi and U. Siemeling in J. Orgmet. Chem. (1995), 500, 175-185. The metal complexes, in particular the chromium complexes, can be obtained in a simple manner by reacting the appropriate metal salts, e.g. metal chlorides, with the ligand anion (e.g. using methods analogous to the examples in DE-A-19710615).

15 Further suitable catalysts D) include metallocenes having at least one ligand which is formed from a cyclopentadienyl or heterocyclopentadienyl and a fused-on heterocycle, with the heterocycles preferably being aromatic and containing nitrogen and/or sulfur. Such compounds are described, for example, in WO 98/22486. These are in
 20 particular dimethylsilanediyl(2-methyl-4-phenylindenyl)(2,5-dimethyl-N-phenyl-4-azapentalene)zirconium dichloride, dimethylsilanediylbis(2-methyl-4-phenyl-4-hydroazulenyl)zirconium dichloride or dimethylsilanediylbis(2-ethyl-4-phenyl-4-hydroazulenyl)zirconium dichloride.

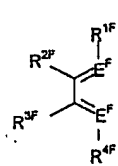
25 Further suitable catalysts D) are systems in which a metallocene compound is combined with, for example, an inorganic oxide which has been treated with zirconium alkoxide and subsequently chlorinated, for example by means of carbon tetrachloride. The preparation of such systems is described, for example, in WO 01/41920.

30 Other suitable catalysts D) include imidochromium compounds in which chromium bears at least one imido group as structural feature. These compounds and their preparation are described, for example, in WO 01/09148.

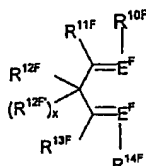
Further suitable components D) include transition metal complexes with a tridentate
 35 macrocyclic ligand, in particular substituted and unsubstituted 1,3,5-triazacyclohexanes and 1,4,7-triazacyclononanes. In the case of this type of catalyst, preference is likewise given to chromium complexes. Preferred catalysts of this type are [1,3,5-tri(methyl)-1,3,5-triazacyclohexane]chromium trichloride, [1,3,5-tri(ethyl)-1,3,5-tri-

azacyclohexane]chromium trichloride, [1,3,5-tri(octyl)-1,3,5-triazacyclohexane]chromium trichloride, [1,3,5-tri(dodecyl)-1,3,5-triazacyclohexane]chromium trichloride and [1,3,5-tri(benzyl)-1,3,5-triazacyclohexane]chromium trichloride.

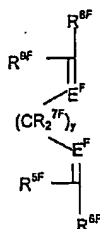
- 5 Further suitable catalysts D) are, for example, transition metal complexes with at least one ligand of the formulae XV to XIX,



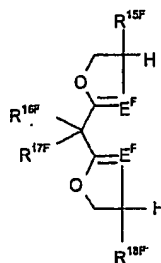
XV



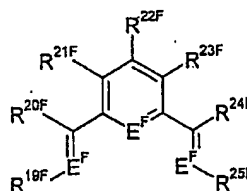
XVI



XVII



XVIII



XIX

- where the transition metal is selected from among the elements Ti, Zr, Hf, Sc, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Pd, Pt and the elements of the rare earth metals. Preference is given to compounds having nickel, iron, cobalt or palladium as central metal.

- 10 E^F is an element of group 15 of the Periodic Table of the Elements, preferably N or P, with particular preference being given to N. The two or three atoms E^F in a molecule can be identical or different.

- The radicals R^{1F} to R^{25F} , which may be identical or different within a ligand system XV to XIX, are as follows:

20

R^{1F} and R^{4F} are each, independently of one another, hydrocarbon radicals or substituted hydrocarbon radicals, preferably hydrocarbon radicals in which the carbon atom adjacent to the element E^F is bound to at least two carbon atoms,

25

R^{2F} and R^{3F} are each, independently of one another, hydrogen, a hydrocarbon radical

or a substituted hydrocarbon radical, where R^{2F} and R^{3F} together may also form a ring system in which one or more heteroatoms may be present,

5 R^{6F} and R^{8F} are each, independently of one another, hydrocarbon radicals or substituted hydrocarbon radicals,

R^{5F} and R^{9F} are each, independently of one another, hydrogen, a hydrocarbon radical or a substituted hydrocarbon radical,

10 where R^{6F} and R^{5F} or R^{8F} and R^{9F} may together also form a ring system,

R^{7F} are each, independently of one another, hydrogen, a hydrocarbon radical or a substituted hydrocarbon radical, where two R^{7F} may together also form a ring system,

15 R^{10F} and R^{14F} are, independently of one another, hydrocarbon radicals or substituted hydrocarbon radicals,

20 R^{11F} , R^{12F} , $R^{12F'}$ and R^{13F} are each, independently of one another, hydrogen, a hydrocarbon radical or a substituted hydrocarbon radical, where two or more geminal or vicinal radicals R^{11F} , R^{12F} , $R^{12F'}$ and R^{13F} may together form a ring system,

25 R^{15F} and R^{18F} are each, independently of one another, hydrogen, a hydrocarbon radical or a substituted hydrocarbon radical,

R^{16F} and R^{17F} are each, independently of one another, hydrogen, a hydrocarbon radical or a substituted hydrocarbon radical,

30 R^{19F} and R^{25F} are each, independently of one another, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, where the organic radicals R^{16F} and R^{25F} may also be substituted by halogens,

35 R^{20F} - R^{24F} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part or SiR^{26F}_3 , where the organic radicals R^{20F} - R^{24F} may also be substituted by halogens and

two vicinal radicals R^{20F} - R^{24F} may also be joined to form a five- or six-membered ring and

5 R^{26F} are each, independently of one another, hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl or alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and two radicals R^{26F} may also be joined to form a five- or six-membered ring,

10 x is 0 or 1, with the complex of the formula (XVI) being negatively charged when x = 0, and

y is an integer from 1 to 4, preferably 2 or 3.

15 Particularly useful transition metal complexes are those having Fe, Co, Ni, Pd or Pt as central metal and containing ligands of the formula (XV). Particular preference is given to diimine complexes of Ni or Pd, e.g.:

20 Di(2,6-di-i-propylphenyl)-2,3-dimethyldiazabutadienepalladium dichloride, di(di-i-propylphenyl)-2,3-dimethyldiazabutadienenickel dichloride, di(2,6-di-i-propylphenyl)dimethyldiazabutadienedimethylpalladium, di(2,6-di-i-propylphenyl)-2,3-dimethyldiazabutadienedimethylnickel, di(2,6-dimethylphenyl)-2,3-dimethyldiazabutadienepalladium dichloride, di(2,6-dimethylphenyl)-2,3-dimethyldiazabutadienenickel dichloride, di(2,6-dimethylphenyl)-2,3-dimethyldiazabutadienedimethylpalladium, di(2,6-dimethylphenyl)-2,3-dimethyldiazabutadienedimethylnickel, di(2-methylphenyl)-2,3-dimethyldiazabutadienepalladium dichloride, di(2-methylphenyl)-2,3-dimethyldiazabutadienenickel dichloride, di(2-methylphenyl)-2,3-dimethyldiazabutadienedimethylpalladium, di(2-methylphenyl)-2,3-dimethyldiazabutadienedimethylnickel, diphenyl-2,3-dimethyldiazabutadienepalladium dichloride, diphenyl-2,3-dimethyldiazabutadienenickel dichloride, diphenyl-2,3-dimethyldiazabutadienedimethylpalladium, diphenyl-2,3-dimethyldiazabutadienedimethylnickel, di(2,6-dimethylphenyl)-azanaphthenepalladium dichloride, di(2,6-dimethylphenyl)azanaphthenenickel dichloride, di(2,6-dimethylphenyl)azanaphthenedimethylpalladium, di(2,6-dimethylphenyl)azanaphthenedimethylnickel, 1,1'-bipyridylpalladium dichloride, 1,1'-bipyridylnickel dichloride, 1,1'-bipyridyl(dimethyl)palladium, 1,1'-bipyridyl(dimethyl)nickel.

35

Particularly useful compounds (XIX) also include those which are described in J. Am. Chem. Soc. 120, p. 4049 ff. (1998), J. Chem. Soc., Commun. 1998, 849, and WO 98/27124. E^F is preferably nitrogen and R^{19F} and R^{25F} in (XIX) are preferably phenyl,

- naphthyl, biphenyl, anthranyl, o-, m-, p-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, -dichlorophenyl or -dibromophenyl, 2-chloro-6-methylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, in particular 2,3- or 2,6-dimethylphenyl, -diisopropylphenyl, -dichlorophenyl or -dibromophenyl and 2,4,6-trimethylphenyl. At the same time, R^F and R^{24F} are preferably hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, benzyl or phenyl, in particular hydrogen or methyl. R^{21F} and R^{23F} are preferably hydrogen and R^{22F} is preferably hydrogen, methyl, ethyl or phenyl, in particular hydrogen.
- Preference is given to complexes of the ligands XIX with the transition metals Fe, Co or Ni, in particular Fe. Particular preference is given to 2,6-diacetylpyridinebis(2,4-dimethylphenylimine)iron dichloride, 2,6-diacetylpyridinebis(2,4,6-trimethylphenylimine)iron dichloride, 2,6-diacetylpyridinebis(2-chloro-6-methylphenylimine)iron dichloride, 2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)iron dichloride, 2,6-diacetylpyridinebis(2,6-dichlorophenylimine)iron dichloride, 2,6-pyridinedicarboxaldehydebis(2,6-diisopropylphenylimine)iron dichloride, 2,6-diacetylpyridinebis(2,4-dimethylphenylimine)cobalt dichloride, 2,6-diacetylpyridinebis(2,4,6-trimethylphenylimine)cobalt dichloride, 2,6-diacetylpyridinebis(2-chloro-6-methylphenylimine)cobalt dichloride, 2,6-diacetylpyridinebis(2,6-diisopropylphenylimine)cobalt dichloride, 2,6-diacetylpyridinebis(2,6-dichlorophenylimine)cobalt dichloride, and 2,6-pyridinedicarboxaldehydebis(2,6-diisopropylphenylimine)cobalt dichloride.

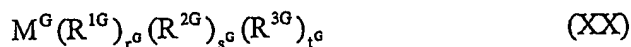
- Iminophenoxide complexes can also be used as catalysts D). The ligands of these complexes can be prepared, for example, from substituted or unsubstituted salicylaldehydes and primary amines, in particular substituted or unsubstituted arylamines.
- Transition metal complexes with pi ligands having one or more heteroatoms in the pi system, for example the boratabenzene ligand, the pyrrolyl anion or the phospholyl anion, can also be used as catalyst D).

- Further complexes suitable as catalyst D) include those which have bidentate or tridentate chelating ligands. In such ligands, for example, an ether function is linked to an amine or amide function or an amide is linked to a heteroaromatic such as pyridine.

- Such combinations of components A) and D) enable, for example, bimodal products to be prepared or comonomers to be generated in situ. Preference is given to using at least one monocyclopentadienyl complex A) in the presence of at least one catalyst D) customary for the polymerization of olefins and if desired, one or more activating compounds C). Here, depending the catalyst combinations A) and D), one more activating compounds C) may be advantageous. The polymerization catalysts D) can

likewise be supported and can be used simultaneously or in any order with the complex A) of the present invention. For example, the monocyclopentadienyl complex A) and the polymerization catalysts D) can be applied together to a support B) or different supports B). It is also possible to use mixtures of various catalysts as component D). The molar ratio of monocyclopentadienyl complex A) to polymerization catalyst B) is usually in the range from 1:100 to 100:1, preferably from 1:20 to 20:1 and particularly preferably from 1:10 to 10:1.

The catalyst system may further comprise, as additional component E), a metal compound of the formula (XX),



where

15

M^G is Li, Na, K, Be, Mg, Ca, Sr, Ba, boron, aluminum, gallium, indium, thallium, zinc, in particular Li, Na, K, Mg, boron, aluminum or Zn,

20

R^{1G} is hydrogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, alkylaryl or arylalkyl each having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

25

R^{2G} and R^{3G} are each hydrogen, halogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, alkylaryl, arylalkyl or alkoxy each having from 1 to 20 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical, or alkoxy with C_1 - C_{10} -alkyl or C_6 - C_{15} -aryl,

30 and

r^G is an integer from 1 to 3

s^G and t^G are integers from 0 to 2, with the sum $r^G + s^G + t^G$ corresponding to the valence of M^G ,

35

where the component E) is not identical to the component C). It is also possible to use mixtures of various metal compounds of the formula (XX).

Among the metal compounds of the formula (XX), preference is given to those in

which

M^G is lithium, magnesium, boron or aluminum and

R^{IG} is C_1 - C_{20} -alkyl.

5

Particularly preferred metal compounds of the formula (XX) are methyllithium, ethyllithium, n-butyllithium, methylmagnesium chloride, methylmagnesium bromide, ethylmagnesium chloride, ethylmagnesium bromide, butylmagnesium chloride, dimethylmagnesium, diethylmagnesium, dibutylmagnesium, n-butyl-n-octylmagnesium, n-butyl-n-heptylmagnesium, in particular n-butyl-n-octylmagnesium, tri-n-hexylaluminum, triisobutylaluminum, tri-n-butylaluminum, triethylaluminum, dimethylaluminum chloride, dimethylaluminum fluoride, methylaluminum dichloride, methylaluminum sesquichloride, diethylaluminum chloride and trimethylaluminum and mixtures thereof. The partial hydrolysis products of aluminum alkyls with alcohols can also be used.

10
15

When a metal compound E) is used, it is preferably present in the catalyst system in such an amount that the molar ratio of M^G from formula (XX) to transition metal from monocyclopentadienyl compound A) is from 2 000:1 to 0.1:1, preferably from 800:1 to 0.2:1 and particularly preferably from 100:1 to 1:1.

20

In general, the catalyst solid together with the further metal compound E) of the formula (XX), which may be different from the metal compound or compounds E) used in the preparation of the catalyst solid, is used as constituent of a catalyst system for the polymerization or copolymerization of olefins. It is also possible, particularly when the catalyst solid does not contain any activating component C), for the catalyst system to further comprise, in addition to the catalyst solid, one or more activating compounds C) which are identical to or different from any activating compounds C) present in the catalyst solid.

25

30

To prepare the catalyst systems of the present invention, preference is given to immobilizing at least one of the components A) and/or C) on the support B) by physisorption or by means of chemical reaction, i.e. covalent binding of the components, with reactive groups of the support surface. The order in which the support component B), the component A) and any component C) are combined is immaterial. The components A) and C) can be added independently of one another or simultaneously or in premixed form to B). After the individual process steps, the solid can be washed with suitable inert solvents such as aliphatic or aromatic hydrocarbons.

35

In a preferred embodiment the monocyclopentadienyl complex A) is brought into contact with the activating compound C) in a suitable solvent, usually giving a soluble reaction product, an adduct or a mixture. The preparation obtained in this way is then brought into contact with the support B), which may have been pretreated, and the solvent is completely or partly removed. This preferably gives a solid in the form of a free-flowing powder. Examples of the industrial implementation of the above process are described in WO 96/00243, WO 98/40419 or WO 00/05277. A further preferred embodiment comprises firstly applying the cation-forming compound C) to the support B) and subsequently bringing this supported cation-forming compound into contact with the monocyclopentadienyl complex A).

The component D) can likewise be reacted in any order with the components A) and, if desired, B), C) and E). Preference is given to bringing D) firstly into contact with component C) and then dealing with the components A) and B) and any further C) as described above. In another preferred embodiment, a catalyst solid is prepared from the components A), B) and C) as described above and this is brought into contact with the component E) during, at the beginning of or shortly before the polymerization. Preference is given to E) firstly being brought into contact with the α -olefin to be polymerized and the catalyst solid comprising the components A), B) and C) as described above subsequently being added.

The monocyclopentadienyl complex A) can be brought into contact with the component(s) C) and/or D) either before or after being brought into contact with the olefin to be polymerized. Preactivation using one or more components C) prior to mixing with the olefin and further addition of the same or different components C) and/or D) after the mixture has been brought into contact with the olefin is also possible. Preactivation is generally carried out at 10-100°C, in particular 20-80°C.

It is also possible for the catalyst system firstly to be prepolymerized with α -olefins, preferably linear C_2 - C_{10} -1-alkenes and in particular ethylene or propylene, and the resulting prepolymerized catalyst solid then to be used in the actual polymerization. The mass ratio of catalyst solid used in the prepolymerization to monomer polymerized onto it is usually in the range from 1:1 to 1:1 000, preferably from 1:1 to 1:200.

Furthermore, a small amount of an olefin, preferably an α -olefin, for example vinylcyclohexane, styrene or phenyldimethylvinylsilane, as modifying component, an antistatic or a suitable inert compound such as a wax or oil can be added as additive

during or after the preparation of the catalyst system. The molar ratio of additives to transition metal compound B) is usually from 1:1 000 to 1 000:1, preferably from 1:5 to 20:1.

- 5 The catalyst systems of the present invention are suitable for the polymerization of olefins and especially for the polymerization of α -olefins, i.e. hydrocarbons having terminal double bonds. Suitable monomers also include functionalized olefinically unsaturated compounds such as acrolein, ester or amide derivatives of acrylic or methacrylic acid, for example acrylates, methacrylates or acrylonitrile, or vinyl esters, 10 for example vinyl acetate. Preference is given to nonpolar olefinic compounds, including aryl-substituted α -olefins. Particularly preferred α -olefins are linear or branched C_2 - C_{12} -1-alkenes, in particular linear C_2 - C_{10} -1-alkenes such as ethene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene or branched C_2 - C_{10} -1-alkenes such as 4-methyl-1-pentene, conjugated and unconjugated dienes 15 such as 1,3-butadiene, 1,5-hexadiene or 1,7-octadiene or vinylaromatic compounds such as styrene or substituted styrene. It is also possible to polymerize mixtures of various α -olefins. Preference is given to polymerizing at least one olefin selected from the group consisting of ethene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and 1-decene.

20 Suitable olefins also include ones in which the double bond is part of a cyclic structure which can have one or more ring systems. Examples are cyclopentene, cyclohexene, norbornene, tetracyclododecene and methylnorbornene and dienes such as 5-ethylidene-2-norbornene, norbornadiene or ethylnorbornadiene.

- 25 Mixtures of two or more olefins can also be polymerized. In contrast to some known iron and cobalt complexes, the monocyclopentadienyl complexes of the present invention display a good polymerization activity even in the case of higher α -olefins, so that their suitability for copolymerization deserves particular emphasis. In particular, the monocyclopentadienyl complexes of the present invention can be used for 30 the polymerization or copolymerization of ethene or propene. As comonomers in the polymerization of ethene, preference is given to using C_3 - C_8 - α -olefins or norbornene, in particular 1-butene, 1-pentene, 1-hexene and/or 1-octene. Preference is given to using monomer mixtures containing at least 50 mol% of ethene. Preferred comonomers 35 in the polymerization of propylene are ethene and/or butene.

The polymerization can be carried out in a known manner in bulk, in suspension, in the gas phase or in a supercritical medium in the customary reactors used for the

polymerization of olefins. It can be carried out batchwise or preferably continuously in one or more stages. High-pressure polymerization processes in tube reactors or autoclaves, solution processes, suspension processes, stirred gas-phase processes or gas-phase fluidized-bed processes are all possible.

5

- The polymerizations are usually carried out at from -60 to 350°C under pressures of from 0.5 to 4 000 bar at mean residence times of from 0.5 to 5 hours, preferably from 0.5 to 3 hours. The advantageous pressure and temperature ranges for carrying out the polymerizations usually depend on the polymerization method. In the case of high-
- 10 pressure polymerization processes, which are usually carried out at pressures of from 1 000 to 4 000 bar, in particular from 2 000 to 3 500 bar, high polymerization temperatures are generally also set. Advantageous temperature ranges for these high-pressure polymerization processes are from 200 to 320°C, in particular from 220 to 290°C. In the case of low-pressure polymerization processes, a temperature which is
- 15 at least a few degrees below the softening temperature of the polymer is generally set. These polymerization processes are preferably carried out at from 50 to 180°C, preferably from 70 to 120°C. In the case of suspension polymerization, the polymerization is usually carried out in a suspension medium, preferably an inert hydrocarbon such as isobutane or a mixture of hydrocarbons, or else in the monomers themselves.
- 20 The polymerization temperatures are generally in the range from -20 to 115°C, and the pressure is generally in the range from 1 to 100 bar. The solids content of the suspension is generally in the range from 10 to 8%. The polymerization can be carried out batchwise, e.g. in stirring autoclaves, or continuously, e.g. in tube reactors, preferably in loop reactors. Particular preference is given to employing the Phillips PF
- 25 process as described in US-A-3 242 150 and US-A-3 248 179. The gas-phase polymerization is generally carried out at from 30 to 125°C.

- Among the abovementioned polymerization processes, particular preference is given to gas-phase polymerization, in particular in gas-phase fluidized-bed reactors, solution
- 30 polymerization and suspension polymerization, in particular in loop reactors and stirred tank reactors. The gas-phase polymerization can also be carried out in the condensed or supercondensed phase, in which part of the circulating gas is cooled to below the dew point and is recirculated as a two-phase mixture to the reactor. It is also possible to use a multizone reactor in which two polymerization zones are linked to
- 35 one another and the polymer is passed alternately through these two zones a number of times. The two zones can also have different polymerization conditions. Such a reactor is described, for example, in WO 97/04015. The different or identical polymerization processes can also, if desired, be connected in series so as to form a poly-

merization cascade, for example in the Hostalen process. A parallel reactor arrangement using two or more identical or different processes is also possible. Furthermore, molar mass regulators, for example hydrogen, or customary additives such as antistatics can also be used in the polymerizations.

5

The monocyclopentadienyl complexes of the present invention and the catalyst systems in which they are present can also be prepared by means of combinatorial synthesis or their polymerization activity can be tested with the aid of combinatorial methods.

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The process of the present invention allows polymers of olefins to be prepared. The term "polymerization" as used here in the description of the present invention encompasses both polymerization and oligomerization, i.e. oligomers and polymers having molar masses M_w in the range from about 56 to 3 000 000 g/mol can be produced by this process.

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Owing to their good mechanical properties, the olefin polymers prepared using the catalyst system of the present invention are particularly useful for the production of films, fibers and moldings.

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The catalyst systems of the present invention give a very productivity in the polymerization of olefins, offer advantages in the work-up of the polymers after the polymerization and lead to significantly fewer problems in respect of catalyst residues in the polymer. The polymers prepared using the catalyst system of the present invention are particularly useful for applications which require a high productivity. In addition, the catalyst systems of the present invention display a very good activity even at a relatively low molar ratio of aluminoxane to transition metal compound and incorporate high levels of comonomer. The catalyst systems are therefor especially well suited for the preparation of ethylene copolymers with a density from 0.89 to 0.93 g/cm³ and with a molecular weight of 20 000 to 140 000 g/mol.

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Examples

The comonomer content of the polymer (% by weight of hexene in the polymer), its methyl side chain content per 1 000 carbon atoms of the polymer chain (CH₃/1 000C) were determined by IR spectroscopy.

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The η value was determined by means of an automatic Ubbelohde viscometer (Lauda PVS 1) using decalin as solvent at 130°C (ISO 1628 at 130°C, 0.001 g/ml of decalin).

The determination of the molar mass distributions and the mean values M_n , M_w and M_w/M_n derived therefrom were carried out by means of high-temperature gel permeation chromatography using a method based on DIN 55672 under the following conditions: solvent: 1,2,4-trichlorobenzene, flow: 1 ml/min, temperature: 140°C, calibration using PE standards.

The density [g/cm^3] was determined in accordance with ISO 1183.

Abbreviations in the table below:

cat.	catalyst
t(poly)	polymerization time
polymer	amount of polymer formed
M_w	weight average molar mass
M_n	number average molar mass
density	polymer density
prod.	productivity of the catalyst in g of polymer obtained per mmol of catalyst (chromium complex) used per hour

All catalyst preparations and handling were carried out under inert gas conditions. All solvents were dried and degassed.

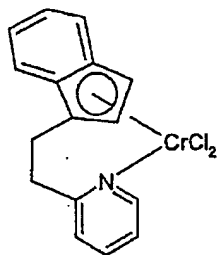
Example 1

1.1. Preparation of 2-[2-(1H-inden-3-yl)ethyl]pyridine (as described by H. Dressler and R.J. Kurland, J. Org. Chem. 29 1 p. 175-178)

43 g (0.47 mol) of 2-vinylpyridine were added to a mixture of 56 ml (0.48 mol) of indene in 40 ml of toluene and 4 g (0.036 mol) of solid potassium tert-butoxide at 60-90°C over a period of 40 minutes. The mixture was then stirred for another 2 hours at 115°C, cooled to room temperature and subsequently neutralized by means of 2 ml of glacial acetic acid. Insoluble constituents were filtered off and the filtrate was distilled under reduced pressure. This gave 42 g of 2-[2-(1H-inden-3-yl)ethyl]pyridine (40%, b.p. 161-163°C at 2 mm).

^1H NMR (CDCl_3): 8.62 (d, 1H); 7.64 (td, 1H); 7.55 (d, 1H); 7.51 (d, 1H); 7.39 (t, 1H), 7.29 (t, 1H); 7.23 (d, 1H); 7.19 (dd, 1H); 6.32 (m, 1H); 3.40 (m, 2H); 3.28 (m, 2H); 3.12 (m, 2H).

1.2. Preparation of (3-(2-pyridylethyl)indenyl)chromium dichloride



A solution of 22.1 g (0.1 mol) of 2-[2-(1H-inden-3-yl)ethyl]pyridine in 470 ml of tetrahydrofuran was cooled to -100°C . 62.5 ml of a 15% strength n-butyllithium solution in hexane (0.1 mol) were slowly added dropwise. After the addition was complete, the reaction mixture was stirred for a further 50 minutes at -100°C . The mixture was subsequently allowed to warm to room temperature. After stirring for another 2 hours, the solution was cooled to -60°C and 38 g (0.1 mol) of chromium trichloride tris(tetrahydrofuran) were added while stirring. The mixture was allowed to warm slowly to room temperature and was subsequently stirred for another 10 hours at room temperature. The reaction mixture was then refluxed for 20 minutes and subsequently cooled to room temperature. The solid which had precipitated was filtered off and washed with hot tetrahydrofuran. The solid was subsequently washed with diethyl ether and dried under reduced pressure. This gave 28.1 g of (3-(2-pyridylethyl)indenyl)chromium dichloride (82%).

Example 2

- a) Pretreatment of support: 100 g of Puralox MG 61 (calcined hydrotalcite) from Condea Chemie, GmbH (now Sasol Chemie) were heated at 180°C for 6 hours.
- b) Application of the catalyst complex to the support: 148.9 mg of the complex from example 1 (82.1 mmol) were admixed with 11.42 ml of a 4.75 M solution of MAO in toluene from Albemarle and the mixture was stirred for 15 minutes. The resulting solution was added over a period of 10 minutes to 6.2 g of the pretreated calcined hydrotalcite and the mixture was stirred for another 60 min. The catalyst was then dried at room temperature at 10^{-3} mbar. This gave a light-green powder.

Example 3

Polymerization

- The polymerization experiments were carried out in a 1 l four-necked flask provided with contact thermometer, stirrer with Teflon blade, heating mantle and gas inlet tube. 15.5 μmol of (3-(2-pyridylethyl)indenyl)chromium dichloride together with 250 ml of toluene were placed in the flask at 40°C under argon. To activate the catalyst, 7.77

mmol of 1.6M MAO solution in toluene were added.

Before introduction of ethylene, 3 ml of hexene were placed in the flask and about 40 l/h of ethylene were subsequently passed through the initial charge for 20 minutes at atmospheric pressure. The remaining amount of hexene (another 8 ml) was introduced via a dropping funnel over a period of 10 minutes.

The reaction was stopped by addition of a mixture of 15 ml of concentrated hydrochloric acid and 50 ml of methanol and the mixture was stirred for another 15 minutes. After addition of another 250 ml of methanol and stirring for 15 minutes, the mixture was filtered, the solid was washed three times with methanol and dried at 70°C. This gave 8.9 g of ethylene-hexene copolymer (activity of the catalyst: 1 735 g/(mmol of Cr·h)) having an M_w of 397 972 g/mol, an M_w/M_n of 3.34, a hexene content of 6.2% and a density of 0.9053 g/cm³.

Example 4

Polymerization

400 ml of isobutane and 2 ml of a triisobutylaluminum solution in heptane (corresponding to 60 mg of triisobutylaluminum) were placed in a 1 l autoclave which had been made inert by means of argon, and 149 mg of the catalyst solid obtained in example 2b) were finally added. Polymerization was carried out at 70°C and an ethylene pressure of 40 bar for 60 minutes. The polymerization was stopped by releasing the pressure and the product was discharged through the bottom valve. This gave 157 g of polyethylene having a density of 0.9228 g/cm³, a bulk density of 412 kg/m³ and a η value of 32.28 dl/g.

Productivity: 1050 g of PE/g of catalyst solid.

Example 5

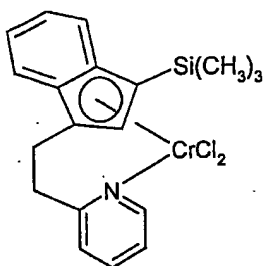
5.1. Preparation of 2-{2-[1-(trimethylsilyl)-1H-inden-3-yl]ethyl}pyridine

2-[2-(1H-inden-3-yl)ethyl]pyridine (14.88g, 0.0637 mol) was dissolved in 190ml of diethylether. The resulting solution was cooled to -90°C and then 15% n-butyllithium in hexane (42.08 ml, 67.3 mmol) added. The resulting mixture was stirred at this temperature for an additional 30 min and then allowed to reach room temperature. After additional stirring for 1 h at room temperature, the mixture was cooled to -90°C and was then treated with a solution of SiMe₃Cl (9.4 ml, 74 mmol) in 10 ml of diethylether. The resulting mixture was allowed to warm to room temperature, and then stirred for 12 h. Then the mixture was first treated with water and then aqueous ammonium chloride solution. The organic phase was separated and the aqueous phase

extracted three times with diethylether. The combined organic phase was washed with brine and dried over MgSO_4 . After filtration, the solvent was removed from the filtrate to give 15.97 g (81%) of 2-{2-[1-(trimethylsilyl)-1H-inden-3-yl]ethyl}pyridine as an oil, which was used in the next stage without separation.

- 5 $^1\text{H-NMR}$ (CDCl_3): 8.63 (d, 1H); 7.62 (dt, 1H); 7.53 (d, 1H); 7.48 (s, 1H); 7.33 (t, 1H); 7.24 (m, 2H); 7.16 (dd, 1H); 6.39 (br s, 1H); 3.44 (br s, 1H); 3.26 (m, 2H); 3.14 (m, 2H); -0.04 (s, 9H).

10 5.2. Preparation of 2-{2-[1-(trimethylsilyl)-indenyl]ethyl}pyridinechromium dichloride



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- A solution of 2-{2-[1-(trimethylsilyl)-1H-inden-3-yl]ethyl}pyridine (15.97 g, 54.5 mmol) in 170 ml of tetrahydrofuran was cooled to -100°C . 15% n-butyllithium in hexane (34 ml, 54.5 mmol) was added and the resulting mixture stirred at this temperature for an additional 1 h. The reaction mixture was allowed to warm up to room temperature (in about 2 h) and then cooled to -60°C . 20.42 g (54.5 mmol) of chromium trichloride tris(tetrahydrofuran) were added, the resulting mixture allowed to warm to room temperature and then stirred for 12 h. Then 90 ml of solvent were removed, the resulting green suspension refluxed for 20 min and then slowly cooled to room temperature. The green precipitate was filtered off and washed twice with diethylether to give 15.6 g of green powder. Recrystallization from a mixture of dichloromethane/diethylether gave 5 g (22%) of 2-{2-[1-(trimethylsilyl)-indenyl]-ethyl}pyridinechromium dichloride as dark green powder.

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Example 6

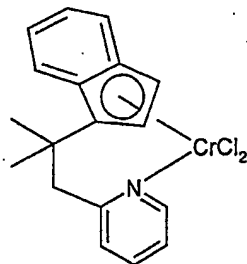
6.1. Preparation of 2-[2-(1H-inden-1-yl)-2-methylpropyl]pyridine

- A solution of α -Picoline (1.97 ml, 20 mmol) in 10 ml of tetrahydrofuran was cooled to -20°C and 15% n-butyl-lithium in hexane (13 ml, 20 mmol) was added during 10 min with stirring. The cooling bath was removed and the solution allowed to stir for 1 h while the temperature rose to room temperature. The resulting mixture was treated with a solution of 1-(1-methylethylidene)-1H-indene (3.12 g, 20 mmol) in 5 ml of tetrahydrofuran (5 ml) with vigorous stirring. The resulting solution was stirred for 14

h and hydrolyzed with 60 ml of 15-% hydrochloric acid. The organic layer was isolated and the aqueous phase washed once with ethyl acetate, then neutralized with aqueous ammonia solution and extracted three times with dichloromethane. The combined organic layers were dried over MgSO_4 , filtered and the solvent removed to give 4.28 g (86%) of 2-[2-(1H-inden-1-yl)-2-methylpropyl]pyridine as an oil. The product was NMR-pure, so no further distillation was necessary.

$^1\text{H-NMR}$ (CDCl_3): 8.55 (dm, 1H); 7.84 (d, 1H); 7.53 (d, 1H); 7.39 (m, 2H); 7.26 (t, 1H); 7.08 (ddd, 1H); 6.70 (d, 1H); 6.11 (t, 1H); 3.32 (br.s, 2H); 3.30 (d, 2H); 1.42 (s, 6H).

6.2. Preparation of 2-[2-(indenyl)-2-methylpropyl]pyridinechromium dichloride



A solution of 2-[2-(1H-inden-1-yl)-2-methylpropyl]pyridine (4.28 g, 17.2 mmol) in 53 ml of tetrahydrofuran was cooled to -100°C . 15% n-butyllithium in hexane (10.7 ml, 17.2 mmol) was added and the resulting mixture stirred at this temperature for an additional 1 h. The reaction mixture was allowed to warm up to room temperature (in about 2 h) and then cooled to -60°C . 6.44 g (17.2 mmol) of chromium trichloride tris(tetrahydrofuran) were added, the resulting mixture allowed to warm to room temperature and then stirred for 12 h. Then 30 ml of solvent were removed, the green precipitate filtered off and washed twice with diethylether to give 3.6 g of green powder. Recrystallization from a mixture of dichloromethane/diethylether gave 2.1 g of 2-[2-(indenyl)-2-methylpropyl]pyridinechromium dichloride as dark green powder.

Example 7

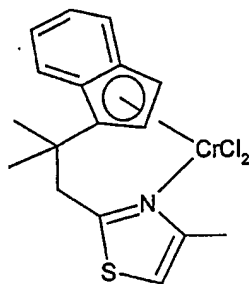
7.1. Preparation of 2-[2-(1H-inden-3-yl)-2-methylpropyl]-4-methyl-1,3-thiazole

A solution of 2,4-dimethyl-1,3-thiazole (3.2 g, 28.1 mmol) in 20 ml of tetrahydrofuran was cooled to -78°C and 15% n-butyl-lithium in hexane (17.5 ml, 28 mmol) was added during 15 min with stirring. The resulting yellow suspension was stirred for 20 min and then a solution of 1-(1-methylethylidene)-1H-indene (4.6 g, 29 mmol) in 5 ml of tetrahydrofuran added with vigorous stirring while the temperature was maintained at -78°C . The reaction mixture was allowed to reach room temperature and for 14 h. The resulting mixture was hydrolyzed with a saturated ammonium chloride solution.

The organic layer was isolated and the aqueous phase extracted three times with dichloromethane. The combined organic layers were dried over MgSO_4 , filtered and the solvent removed. The crude product was further purified by column chromatography over silica. At the beginning a 5/1 hexane/ethyl acetate elution mixture was used (for the separation from 1-(1-methylethylidene)-1H-indene). Then, the elution mixture was changed to 1/1 hexane/ethyl acetate. After removal of the solvent 5.62 g (74 %) of 2-[2-(1H-inden-3-yl)-2-methylpropyl]-4-methyl-1,3-thiazole was obtained as an oil.

$^1\text{H-NMR}$ (CDCl_3): 7.74 (d, 1H); 7.53 (d, 1H); 7.35 (t, 1H); 7.25 (t, 1H); 6.64 (d, 1H); 6.23 (t, 1H); 3.51 (s, 2H); 3.34 (d, 2H); 2.43 (d, 3H); 1.47 (s, 6H).

7.2. Preparation of 2-[2-(indenyl)-2-methylpropyl]-4-methyl-1,3-thiazolechromium dichloride



A solution of 2-[2-(1H-inden-3-yl)-2-methylpropyl]-4-methyl-1,3-thiazole (5.62 g, 21 mmol) in 70 ml of tetrahydrofuran was cooled to -100°C . 15% n-butyllithium in hexane (13.7 ml, 22 mmol) was added and the resulting mixture stirred at this temperature for an additional 1 h. The reaction mixture was allowed to warm up to room temperature (in about 2 h) and then cooled to -60°C . 8.6 g (23 mmol) of chromium trichloride tris(tetrahydrofuran) were added, the resulting mixture allowed to warm to room temperature and then stirred for 12 h. The green precipitate was filtered off and washed twice with diethylether to give 4.3 g of green powder. Recrystallization from a mixture of dichloromethane/diethylether gave 2.7 g (33 %) of 2-[2-(indenyl)-2-methylpropyl]-4-methyl-1,3-thiazolechromium dichloride as dark green crystals.

Example 8

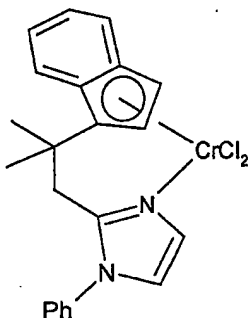
8.1. Preparation of 2-[2-(1H-inden-3-yl)-2-methylpropyl]-1-phenyl-1H-imidazole

A solution of 1.58 g 2-methyl-1-phenyl-1H-imidazole (10 mmol) in 15 ml of tetrahydrofuran was cooled to -78°C and 6.25 ml of 15% n-butyl-lithium in hexane (10 mmol) were added. The resulting mixture was stirred for an additional 20 min and then treated with a solution of 1.56 g 1-(1-methylethylidene)-1H-indene (10 mmol) in

5 ml tetrahydrofuran with vigorous stirring while the temperature was maintained at -78°C . The reaction mixture was allowed to reach room temperature, stirred for 14 h and hydrolyzed with saturated ammonium chloride solution. The organic layer was isolated and the aqueous layer was extracted three times with dichloromethane. The organic layers were dried over MgSO_4 , filtered and the solvent removed. The crude product was purified by column chromatography with silica as stationary phase. At the beginning a 5/1 hexane/ethyl acetate elution mixture was used (for the separation from 1-(1-methylethylidene)-1H-indene). Then, the elution mixture was changed to 1/1 hexane/ethyl acetate. After removal of the solvent 2.13 g (69%) of 2-[2-(1H-inden-3-yl)-2-methylpropyl]-1-phenyl-1H-imidazole was obtained as an oil.

$^1\text{H-NMR}$ (CDCl_3): 7.41-7.37 (m, 5H); 7.16 (d, 1H); 7.14-7.07 (m, 3H); 6.97 (d, 1H); 6.15 (t, 1H); 3.19 (d, 2H); 3.17 (s, 2H); 1.35 (s, 6H).

8.2. Preparation of 2-[2-(indenyl)-2-methylpropyl]-1-phenyl-imidazolechromium dichloride



A solution of 0.71 g 2-[2-(1H-inden-3-yl)-2-methylpropyl]-1-phenyl-1H-imidazole (2.26 mmol) in 10 ml of tetrahydrofuran was cooled to -100°C . 15% n-butyllithium in hexane (1.48 ml, 2.37 mmol) was added and the resulting mixture stirred at this temperature for an additional 1 h. The reaction mixture was allowed to warm up to room temperature (in about 2 h) and then cooled to -60°C . 0.9 g (2.4 mmol) of chromium trichloride tris(tetrahydrofuran) were added, the resulting mixture allowed to warm to room temperature and then stirred for 12 h. Then the solvent was removed and the residue extracted with dichloromethane. After removal of the solvent from the extract, the crude product was recrystallized from a 5/1 mixture of dichloromethane/diethylether to give 0.37 g (38 %) of 2-[2-(indenyl)-2-methylpropyl]-1-phenyl-imidazolechromium dichloride as a green-blue crystals.

Example 9

Polymerization

Polymerization was carried out at 40°C under argon in a 1 l four-neck flask provided with contact thermometer, stirrer with Teflon blade, heating mantle and gas inlet tube.

The appropriate amount of MAO (10% strength solution in toluene; Cr:Al 1:500) was added to a solution of the amount indicated in table 2 of the respective complex in 250 ml of toluene and the mixture was heated to 40°C on a water bath. In the case of the copolymerisation (see table 2), shortly before introduction of ethylene, 3 ml of hexene were placed in the flask and a further amount of hexene (see table 2) was introduced via a dropping funnel over a period of 15 minutes after introduction of the ethylene. Ethylene was subsequently passed through the flask at a flow rate of about 20-40 l/h at atmospheric pressure (both for homo- and copolymerisations). After the time indicated in table 2 under a constant ethylene flow, the polymerization was stopped by addition of methanolic HCl solution (15 ml of concentrated hydrochloric acid in 50 ml of methanol). 250 ml of methanol were subsequently added and the resulting white polymer was filtered off, washed with methanol and dried at 70°C.

The catalysts of this invention show a particularly interesting polymerization behavior. In the ethylene homopolymerizations they give polymers with a broader molecular weight distribution, which enhances the processing properties. In the case of the ethylene copolymerizations, the molecular weight distribution of the obtained copolymers, which are in general easier to process than HDPE, is very narrow, which results in enhanced mechanical properties. All catalysts readily incorporate high levels of comonomer.

In the case of A is of formula (IIIb) (catalyst of examples 7 and 8) the homopolymers and copolymers have almost the same molecular weight, which indicates that the comonomer does not or only slightly effect the termination of the polymerization. In polymerizations with metallocenes, such as zirconocene dichloride, comonomers usually lead to a significant reduction of the molecular weight of the polymer.

Table 2: Polymerization results

cat. of example	Amount of cat. [mg]	Hexen	t(poly) [min]	Polymer [g]	Prod. [g/mmol Cr h]	M _w [g/mol]	M _w /M _n	CH ₃ /1000C	Density [g/cm ³]
5	31.3	no	30	20.4	1303	123648	6.63	4.9	n.d.
5	18.1	7	20	11.3	1877	55033	3.11	11.8	0.92
6	23.7	no	20	5.74	726	76667	3.75	1.5	0.9572
6	22.1	6	15	10.3	1865	49946	2.61	11.3	0.9342
7	10.5	9	30	4.4	328	7528	2.41	12	n.d.
8	6.3	no	12	7.7	2666	52403	3.96	1.8	0.9653
8	11.9	8	20	16.9	1859	47257	2.44	23.1	0.9087